

CUSP CONDITIONS AND PROPERTIES AT THE NUCLEUS
OF LITHIUM ATOMIC WAVE FUNCTIONS

by

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ABSTRACT

The dependence of the point properties at the nucleus, electron density ($Q^e(0)$) and spin density ($Q^s(0)$), on the nuclear cusp is examined for lithium atomic configuration interaction (CI) wave functions. Several series of CI wave functions with 18 and fewer terms are studied. Importance of the triplet core spin function to $Q^s(0)$ is substantiated.

Necessary, but not sufficient, spin and electron integral cusp conditions are applied as linear constraints. For the functions studied, $Q^s(0)$ improves on applying the spin cusp constraint if the free variational spin cusp is greater than $-Z$, but becomes worse otherwise. The electron cusp constraint invariably overcorrects $Q^e(0)$. The effect of necessary off-diagonal weighting constraints is also examined. No obvious trends could be found. It is concluded that forcing CI functions with a small number of terms to satisfy necessary diagonal or off-diagonal integral cusp conditions has very limited usefulness. A good $Q^s(0)$ can be obtained without constraining by (1) including triplet core spin terms. (2) optimizing orbital exponents.

Sufficient nuclear cusp constraints are developed for CI wave functions. The generalized cusp-satisfying CI function has multiconfigurational SCF form with the correct cusp for each orbital. Sample calculations with a small basis set are presented. These simple functions give extremely good $Q^S(0)$ expectation values but convergence of $Q^S(0)$ with respect to basis set size is yet to be tested. The most interesting discovery is the appearance of Dirac δ -like correction basis orbitals from energy minimization of the orbital exponents.

A scheme is depicted classifying previous and present work on cusp constraints in terms of necessity and/or sufficiency.

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CHAPTER I

PRELIMINARIES

1.1 Introduction

The postulates of quantum mechanics state that to describe a system mathematically one needs to decide on a Hamiltonian for that system and then to solve the corresponding Schrödinger equation. Instead of the true Hamiltonian which can rarely be deduced, one uses the non-relativistic, spinless, time-independent Hamiltonian in many problems of molecular physics or quantum chemistry. Moreover, for molecules, the Born-Oppenheimer approximation is usually used to parametrize the nuclear coordinates. This type of simplified Hamiltonian will be implied throughout this thesis. Solutions of the resulting (simplified) Schrödinger equation will be called exact. These exact wave functions contain all the information needed to calculate any observable of the system by using the appropriate Hermitian operator. Such a procedure will yield, what will be called, exact expectation values.*

* Note that experimentally derived values of observables are sometimes adjusted to yield an experimental estimate for the exact value. For example, the relativistic contribution to the true energy is usually subtracted from the true energy giving the exact energy.

The complexity of many-body interactions makes exact analytic solution of the simplified Schrödinger equation impossible save for a small number of two and three particle systems. There are two general procedures that can be followed at this stage.

Either the Hamiltonian may be simplified further in a way to allow exact solution of the approximate Schrödinger equation--for example, the Hartree-Fock method, or approximate methods may be used to solve the exact Schrödinger equation--for example, series expansion of the solution. Often the two procedures are combined. The solutions from both routes are referred to as approximate wave functions.

In either case energy is almost always used as the criterion for obtaining the wave function. This is because there is an easily applied minimum energy principle. The true ground state is determined uniquely by the lowest eigenvalue of the exact Hamiltonian. The energy, E , of an approximate wave function, ψ , approaches the exact energy as ψ becomes more and more similar to the exact wave function ψ_0 . This is true for other observables also. But they do not necessarily approach their exact values monotonically. Here lies a problem:

the use of energy as a criterion for an approximate wave function does not always ensure reliable expectation values of operators other than the Hamiltonian. This is especially true for point-properties--those properties like the hyperfine splitting, or electron density at the nucleus--which depend on the value of the wave function at a single point in space.

Can reliable expectation values be calculated? There are two distinct approaches to this problem. First, extremely accurate approximate wave functions can be calculated. These must be essentially exact to be sure of obtaining accurate expectation values. The effort needed to obtain such an accurate wave function rapidly increases beyond feasibility with the number of particles. Thus only the hydrogen, helium and lithium atoms and the H_2^+ molecule have been described well enough for the accurate prediction of all (nonrelativistic) properties. To make reliable estimates of properties of more interesting species, such as transition metal complexes, or even small-sized organic compounds seems out of the question at present.

Now for a moment contrast these accurate wave functions with simpler types. Simple wave functions, though not necessarily giving dependable property

values when determined by the energy criterion are easy to construct and easy to calculate (comparatively speaking). Of course their complexity also grows tremendously with the number of particles, but can be lessened by careful application of chemical intuition--difficult to do for the more complicated accurate wave functions. The second approach--the one partially explored in this thesis--utilizes the simplicity of these smaller, less accurate wave functions, together with the existence of other criteria as well as energy for wave function determination, to arrive at a reliable method for calculating atomic and molecular properties. These other criteria include known characteristics, theoretical or experimental, which the exact wave function must exhibit. The quantum-mechanical virial theorem, the hypervirial theorems, the cusp conditions, experimentally known expectation values and the vanishing of net forces are conditions that can aid the characterization of an approximate wave function. Naturally only the exact wave function will satisfy all possible conditions. The usual procedure is to force fulfilment of those conditions affecting the property one wishes to calculate. Different properties will have a different set of

conditions^{*}. The parameters in the functional form chosen to approximate the exact wavefunction are minimized with respect to energy while being constrained to satisfy the desired set of conditions. This is the idea behind the quantum-chemical theory of constraints.

1.2 Object of this work

The work reported in this thesis will test the serviceability of nuclear cusp constraints as aids to make simple approximate wave functions yield good point properties at the nucleus. The lithium atom has been chosen as the system to be investigated for the following reasons:

- (i) Several accurate treatments for lithium are available^{5, 6, 7}
- (ii) The system is accessible experimentally.
8, 9, 10, 11, 12
- (iii) The lithium atom has correlation phenomena characteristic of more complicated systems but is simple enough to reveal the results of the method of constraints without undue computational problems.

Thus, properties of constrained simple lithium functions can be compared with results of both accurate calculations

^{*} For instance, constraining the net forces to vanish, satisfaction of the hypervirial theorems; and forcing the correct cusp behavior should improve calculated force constants, transition probability calculations and contact properties respectively [1, 2, 3, 4] .

and/or experiment allowing a meaningful assessment of the usefulness of nuclear cusp constraints.

1.3 Survey of following chapters

Chapter II consists of background material necessary for understanding why the present work was undertaken. Cusp and coalescence conditions are defined and their applicability to approximate wave functions explained.

The effects on spin and electron density at the nucleus, of forcing approximate configuration interaction wave functions to satisfy integral cusp conditions are presented in Chapter III. Several approaches are described.

Sufficient conditions for ensuring a correct cusp are developed and applied to approximate lithium wave functions in Chapter IV.

Chapter V summarizes the work presented in Chapters III and IV. A scheme classifying cusp conditions and constraints with respect to necessity and sufficiency is tabled.

Appendix A is a list of atomic units used in this work. Definitions and forms of certain basic types of approximate wave functions are presented

in Appendix B. Knowledge of these types is assumed in the text. Methods for applying linear constraints to variationally determined approximate wave functions are outlined in Appendix C. Appendix D discusses the integrals needed in this work and Appendix E contains the description and properties of the complete series of functions defined in Section 3.3.

CHAPTER II

BACKGROUND

2.1 Review of 2S ground state lithium atomic wave functions and contact properties

To understand the reasons for development and application of special constraint techniques to calculate nuclear point properties, a look at some of the past work on lithium wave functions is necessary. No attempt to cover the vast literature is made but important aspects pertaining to the problem will be briefly discussed. A collection of some of the more significant calculations is presented in Table I.* Entries are energy ordered--the best at the bottom. A glance at the table reveals that wave functions so ordered--with energy as a criterion of accuracy--are not in the same sequence when the spin density at the nucleus, $Q^S(0)$, is a criterion. The difficulties in calculating both $Q^S(0)$ and the corresponding electron density, $Q^e(0)$,

* Other workers--see [13, 14, 15, 16, 17] --have also tabulated lithium groundstate calculations from the literature. References [5, 6, 18, 19, 20, 21, 22, 23, 24, 25, 26] contain calculations that have appeared in the literature since Lunell's tabulation [17] in 1968.

Table I. Representative wave functions from the literature for the lithium 2S groundstate.

Description of wave function	Reference	Energy	Spin density at the nucleus			Electron density at the nucleus		
			$Q^s(0)$	% error ^a	Refer- ence	$Q^e(0)$	% error ^b	Refer- ence
1 limited CI, including functions $e^{-\delta r}$ where $\delta = 1.75, 3.5, 7.0$	27	-7.431849	0.2284	+ 1.3	27			
2 analytical HF	28	-7.432727	0.1667	+27.9	29	13.8203	+0.1	29 ^c
3 UHF	29	-7.432751	0.2248	+ 2.8	29	13.8204	+0.1	29 ^c
4 PUHF of Sachs ²⁹	17	-7.432768	0.1866	+19.3	17			
5 EHF (projected)	20	-7.432813	0.2412	- 4.3	20			
6 open shell, 2 determin- ants, σ , spin function	30	-7.4436	0.3002	-29.8	31	13.5193	+2.3	e
7 open shell, 3 determin- ants, (spin optimized)	32,33	-7.4436	0.2417 ^d	- 4.5	13	13.5240	+2.2	e
8 open shell, SEHF, 2 determinants, σ , spin function	17	-7.447529	0.2055	+11.2	17			o

Table I. Representative wavefunctions from the literature for the lithium $2s$ groundstate.
(continued)

	Description of wave function	Reference	Energy	Spin density at the nucleus			Electron density at the nucleus		
				$Q^s(0)$	% error ^a	Reference	$Q^e(0)$	% error ^b	Reference
9	open shell, SEHF, 3 determinants (spin optimized)	17	-7.447536	0.2265	+ 2.1	17			
10	G1-EHF (projected)	21	-7.447560	0.2095	+ 9.4	21	13.864	-0.2	21
11	EHF (spin-optimized)	24,25	-7.447565	0.2265	+ 2.1	24,25	13.8646	-0.2	25
12	s-type basis, 330 term CI (no r_{ij})	23	-7.448520	0.2278	+ 1.5	23			
13	s,p-type basis, 310 term CI (no r_{ij})	23	-7.472680	0.2398	- 3.7	23			
14	scaled 208-term CI (no r_{ij}) with 2 non-linear parameters	34	-7.47369						
15	45 term CI (no r_{ij}), STO basis	35	-7.47710	0.2065	+10.7	13	13.8661	+0.2	36
16	15 term correlated function, Θ , spin function	37	-7.4771						

Table I. Representative wave functions from the literature for the lithium 2S groundstate.
(continued)

	Description of wave function	Reference	Energy	Spin density at the nucleus			Electron density at the nucleus		
				$Q^S(0)$ % error ^a	Refer- ence		$Q^e(0)$ % error ^b	Refer- ence	
17	60 term correlated function, Θ , spin function	6	-7.478010	0.2405	- 4.0	6	13.8327	0.0	38
18	100 term correlated function (spin optimized)	6	-7.478025	0.2313	0.0	6	13.8341	---	38
19	Bruckner-Goldstone Diagrammatic Perturbation	5	-7.478 ± 0.002	0.230 ± 0.002	0.0	5			
20	Exact (Experimental $Q^S(0)$)	39	-7.478069	0.2313	---	8 ^f			

$$^a\% \text{ error} = \frac{Q^S(0) (\text{experimental}) - Q^S(0) (\text{calculated})}{Q^S(0) (\text{experimental})} \times 100\%$$

$$^b\% \text{ error} = \frac{Q^e(0) (\text{Larsson, \#18}) - Q^e(0) (\text{calculated})}{Q^e(0) (\text{Larsson, \#18})} \times 100\%$$

^cCalculated from data in reference.

^dCalculated in this work to be $Q^S(0) = 0.2425$.

^eCalculated in the course of this work.

^fSee reference [40] .

are evident from the work of Jacobs²³ and Larsson.⁶ * Jacobs studied the convergence properties of configuration interaction (CI) wave functions and found erratic values of $Q^S(0)$ for Li and $Q^e(0)$ for He for various expansions converging in energy. Even Larsson's 100 term correlated function^{**}, the most accurate lithium groundstate function available, has not converged in these particular properties because another 100 term correlated function, identical in energy, gives a $Q^e(0)$, $Q^S(0)$ different from the values listed in Table I, by 0.07% and 0.1% respectively. For larger systems errors in $Q^S(0)$ of 25-50% seem to be common. See, for example, the calculations on boron, carbon, nitrogen, oxygen and fluorine by Schaefer et al.⁴¹ Some technique for systematically calculating such point properties is clearly needed, especially for larger systems where formation of accurate correlated functions becomes virtually impossible. Cusp constraints may provide a method.

First of all, for what is the spin density, $Q^S(0)$, useful? It provides an important contribution

* From results communicated to Professor D. P. Chong.

** A brief description of various wave function approximations is given in Appendix B.

to the hyperfine interaction energy. This type of interaction arises from the coupling of electronic and nuclear electric and magnetic fields. The resultant splitting of energy levels can be accurately measured for alkali metal atoms in atomic beam magnetic resonance experiments. Experimental results from the alkali metal group can be exploited as a check in developing theoretical techniques of forming wave functions. Improved techniques will then enable theoretical analyses of more complex systems where experiments are not so easily interpreted.

The hyperfine energy^{*}, ΔE_{hfs} , has major contributions from Fermi contact, magnetic dipole-dipole, and electric quadrupole interactions. For an S-state only the Fermi contact term, describing electronic spin interactions at or within the nucleus, is non-zero and

$$\Delta E_{\text{hfs}} = h \Delta \mathcal{V} = \frac{8\pi}{3} \frac{(2I+1)}{I} \mu_e \mu_N Q^s(0) \quad (2.1.1)$$

where

$$Q^s(0) = \left\langle \frac{1}{S} \sum_{i=1}^N \mathcal{S}_{z_i} \delta(\underline{r}_i) \right\rangle. \quad (2.1.2)$$

* See more complete outlines and further references in [41, 42].

μ_N , μ_e are the magnitudes of the magnetic moments of the nucleus and an electron respectively; I is the nuclear spin and $\delta(r)$, the Dirac delta function. For Li^7

$$\Delta \nu = 803.512 \text{ Mc/sec} \quad [8].$$

Substituting the accepted values $I_{\text{Li}^7} = 3/2$,

$\mu_N = 3.256310$ nuclear magnetons⁴³, $\mu_e = 1.00116$ Bohr magnetons, into (2.1.1) one obtains the experimental spin density

$$Q^S(0) = 0.2313 a_0^{-3} \quad \text{in atomic units.}$$

The quantity, $Q^S(0)$, is the greatest source of error in theoretical hyperfine calculations for light atoms. The reason for this is the inadequacy of approximate wave functions to describe in detail correlation effects and core polarization.

The correlation problem is concerned with the description of the instantaneous repulsions among electrons. Techniques of formulating approximate wave functions must attempt to deal with this to obtain helpful results, especially in problems of interest to chemists. The correlation energy, E_{corr} ,

defined as the difference between the Hartree-Fock (HF) energy, E_{HF} , of a system and the exact energy, E ,

$$E_{\text{corr}} = E_{\text{HF}} - E \quad (2.1.3)$$

provides a measurement of the interaction. E_{HF} is chosen as a reference because the HF method neglects short-range interactions completely; each electron is assumed to move in a potential created by average movements of all other electrons. Consequently an electron never experiences direct repulsive forces in a HF function. (Application of the Pauli principle by antisymmetrizing the function helps somewhat, though, automatically including correlation between electrons of the same spin). Consider now the specific case, the lithium ^2S ground state. Its HF function can be written

$$\Psi_{\text{HF}} = \mathcal{A} [\varphi_{1s}(1)\alpha(1) \varphi_{1s}(2)\beta(2) \varphi_{2s}(3)\alpha(3)] \quad (2.1.4)$$

in terms of functions of atomic coordinates, φ_i , the usual spin functions α , β and \mathcal{A} , the antisymmetrization operator. Since the 1s contributions cancel exactly, only the 2s orbital contributes

to the spin density (real orbitals assumed)

$$Q_{HF}^S(0) = \varphi_{2s}^2(0), \quad (2.1.5)$$

and provides but 72% of the experimental value (Table I). One might conclude that this result is due to lack of correlation, but there is another important effect--core polarization.*

Exchange forces are more attractive between electrons with the same spin than electrons with different spins. The unpaired 2s electron thus exerts a different force on each core electron and so the K shell orbitals should also be different--that is there should be a split K shell. But the HF method forces the functional form of the α and

β spin core orbitals to be the same. In the unrestricted Hartree-Fock (UHF) method** this particular restriction is relaxed,

$$\psi_{UHF} = A[\varphi_{1s}(1)\alpha(1)\varphi'_{1s}(2)\beta(2)\varphi_{2s}(3)\alpha(3)], \quad (2.1.6)$$

* Sometimes referred to as exchange, or spin, polarization.

** The UHF method is more correctly referred to as the spin-polarized Hartree-Fock method [17].

allowing polarization of the core orbitals by the unpaired spin. Now the K shell can contribute to the spin density;

$$Q_{UHF}^s(0) = \varphi_{1s}^2(0) - \varphi'_{1s}{}^2(0) + \varphi_{2s}^2(0) \quad (2.1.7)$$

and one can see the spectacular improvement from HF \rightarrow UHF in Table I. But ψ_{UHF} is no longer an eigenfunction of the total spin. A small quartet contribution exists. Since spin operators commute with the non-relativistic Hamiltonian, and since a spin dependent property is being calculated it is desirable from a physical viewpoint that a wave function have sharp spin. Perhaps it is this lack of sharp spin in UHF functions that causes tremendous errors--even the wrong sign--in spin densities of certain systems.⁴⁰ If the quartet component is annihilated from a lithium ground state UHF function the spin projected unrestricted Hartree-Fock (PUHF) function--a pure doublet state--is obtained (for Li 2S , still), but it has a poorer spin density (Table I). The quartet component has a non-negligible contribution. An improvement to the PUHF procedure is to project a UHF-type function and then minimize the

energy. Goddard²¹, Kaldor, Schaefer and Harris²⁰ have obtained reasonable, but still erratically behaving spin densities by applying this method--called the spin-extended Hartree-Fock (SEHF) technique--to lithium. $Q^S(0)$ is dependent upon the basis set used in these calculations.

Expansions such as configuration interaction (CI) or correlated functions can describe correlation in principle but sheer technical problems have prevented accurate calculations on systems larger than lithium by means of these approaches. Brueckner-Goldstone many-body perturbation theory does provide a well-defined procedure for calculating wave functions and properties to any desired accuracy. However, it also becomes unwieldy for systems more complex than the first row elements.

Separation of core polarization from correlation effects is difficult for approximate functions. Radial, or 'in-out', correlation can appear to split the core when small basis sets are used, giving one core electron a slightly different probability distribution from the other. Chang, Pu and Das⁵ estimate by the many-body perturbation approach that correlation and core polarization contribute 15%

and 80% respectively of the difference between the HF and exact spin densities. Core polarization seems to be an important attribute to build into an approximate function.

The existence of two degenerate spin functions for doublet spin states of three electrons further complicates the computational problem. These functions are usually designated

$$\begin{aligned}\Theta_1 &= \alpha\beta\alpha - \beta\alpha\alpha = (\alpha\beta - \beta\alpha)\alpha \\ \Theta_2 &= 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha\end{aligned}\tag{2.1.8}$$

Θ_1 , corresponding to the coupling of a singlet core with the doublet valence shell, and Θ_2 , a triplet core with the doublet valence shell. The most general three electron doublet function can be written as the linear combination

$$\Theta = a_1\Theta_1 + a_2\Theta_2.\tag{2.1.9}$$

Θ_1 would be expected to describe a more stable core and indeed Θ_2 has a small effect on energy.^{14, 30, 44} For a fully optimized function, however, $a_2 \neq 0$. More important in the present context,

a_2 has a profound effect on spin density^{6, 17, 24, 25}, present work perhaps by improving the description of core polarization. The projection operator used in PUHF or SEHF functions fixes the ratio a_1/a_2 to a value not necessarily the best for energy or other properties. Recently both Ladner and Goddard²⁵, Kaldor and Harris²⁴ have overcome this restriction in their spin-optimized SEHF functions. Dependence of $Q^S(0)$ on Θ_2 may be seen in Table I. The difficulty need not occur in CI or correlated expansions since a_1/a_2 is implicitly optimized in the secular equations.

If an accurate spin density is desired the neglect of relativistic effects must be examined. These effects should be greatest near the nucleus where an electron has maximum kinetic energy and hence might be important for Fermi contact interactions. A good discussion of relativistic corrections is presented by Tterlikkis, Mahanti and Das.⁴⁵ Solving the Dirac-Hartree-Fock (DHF) relativistic equations for the alkali series enabled the correction $Q_{DHF}^S(0) - Q_{HF}^S(0)$ to be determined. Their results indicate that relativistic corrections are small for lithium (0.2%), sodium (0.7%) and potassium (2%).

Electron density

$$Q^e(0) = \left\langle \sum_{i=1}^N \delta(\underline{r}_i) \right\rangle \quad (2.1.10)$$

is needed to express the isomer shift in Mössbauer spectroscopy.⁴⁶ Although core polarization is not so important, since orbital contributions are summed (in contrast to $Q^s(0)$), the basic difficulties of calculating a point property remain. Discussion of theoretical conditions that, if imposed on approximate functions, might improve these properties are now presented.

2.2 What are cusp and coalescence conditions?

Consider the usual (non-relativistic, time-independent) Hamiltonian in atomic units* for a system of N charged particles:

$$H = T + V \quad (2.2.1)$$

where

$$T = - \sum_{i=1}^N \frac{1}{2m_i} \nabla_i^2 ; \quad V = \sum_{i<j}^N \frac{z_i z_j}{r_{ij}} .$$

T , V , are the kinetic and potential energy operators:

m_i , z_i , the mass and charge of the i^{th} particle.

The Coulomb potential contains singularities at the set of points $\{r_{ij}=0\}$, that is, at the coalescence

* See Appendix A.

of any two (or more) particles. The eigenfunctions of H belong to Hilbert space and must be continuous (save for a finite number of points), square integrable, and bounded everywhere.⁴⁷ Because an exact wave function must be finite, even at the singular points of the Coulomb potential, it must fulfil the conditions known as coalescence conditions.² Coalescence conditions are referred to as cuspl conditions for the case when the wave function has no node at the point of coalescence.

To illuminate the preceding remarks examine an exact one-electron hydrogenic $1s$ wave function.⁴⁸

$\psi_{1s}(r) = N \exp(-Zr)$ where N is the normalization constant and Z , the atomic number. ψ is continuous everywhere but not differentiable since the derivatives $\frac{\partial \psi}{\partial x}$, $\frac{\partial \psi}{\partial y}$, $\frac{\partial \psi}{\partial z}$, do not exist at $r = 0$, the coalescence of the electron with the nucleus. However there is a cusp--a discontinuity in the slope--described by the cusp condition,

$$\left(\frac{\partial \psi}{\partial r} \right)_{r=0} = -Z \psi(0) ,$$

at the only point of coalescence ($r = 0$). All hydrogenic wave functions satisfy this relationship but the coalescence condition for non- s states is

trivial. Any well-behaved eigenfunction of a Hamiltonian must satisfy the coalescence conditions. The ratio $H\psi/\psi$ is then constant and does not contain singularities when ψ is an exact eigenfunction of H .^{49, 50} The following distinctions are emphasized to keep terminology clear in the remainder of the thesis:

1. A cusp of a function, $f(x)$, is the point, $f(x_0)$, at a discontinuity of the slope, $f'(x)$, where $f(x)$ changes its direction. It is also associated with a value: $f'(x_0)/f(x_0)$.
2. A coalescence condition is any mathematical relationship which an exact wave function must satisfy at one of its cusps.
3. A cusp condition is a case of a coalescence condition when the wave function has no node at the singularity.
4. Coalescence is the spatial coincidence of two or more particles. Only the two particle case is considered in this work. When the particles are both electrons it is electron-electron coalescence; when one is an electron, the other a

nucleus, it is electron-nucleus, or nuclear coalescence.

The cusp and coalescence conditions for molecular and atomic wave functions will now be reviewed.

2.3 Theory of coalescence conditions for exact wave functions

Kato⁴⁷ derived, for an N-electron, spinless, atomic wave function, the differential cusp conditions

$$\left(\frac{\partial \hat{\psi}(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)}{\partial r_1} \right)_{r_1=0} = -Z \psi(0, \underline{r}_2, \dots, \underline{r}_N) \quad (2.3.1)$$

for electron-nucleus coalescence

$$\text{and} \left(\frac{\partial \hat{\psi}(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)}{\partial r_{12}} \right)_{r_{12}=0} = \frac{1}{2} \psi(\underline{r}, \underline{r}, \underline{r}_3, \dots, \underline{r}_N) \quad (2.3.2)$$

for electron-electron coalescence. Here Z is the atomic charge of the nucleus in atomic units; $\hat{\psi}$ is the average of ψ about a small sphere with center at the coalescing particles; and $\underline{r} = (\underline{r}_1 + \underline{r}_2)/2$. A nonrelativistic Hamiltonian and the heavy-nucleus approximation were used in Kato's derivation as well as the assumption that only two particles were coalescing. Steiner⁵¹ used the same assumptions and obtained cusp conditions for the probability or, electron,

density--the diagonal element of the first order density matrix.

$$\left(\frac{\partial \rho}{\partial r}\right)_{r=0} = -2Z\rho(0) \quad (2.3.3)$$

Equivalent integrated forms of Kato's cusp conditions given by Bingel, who extended them to molecules⁴⁸ and subsequently proved them rigorously,⁵² are:

$$\begin{aligned} \psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) &= \psi(0, \underline{r}_2, \dots, \underline{r}_N) (1 - Z_\alpha r_1) \\ &+ \underline{r}_1 \cdot \underline{a}(\underline{r}_2, \dots, \underline{r}_N) + O(r_1^2) \end{aligned} \quad (2.3.1a)$$

and

$$\begin{aligned} \psi(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) &= \psi(\underline{r}_1, \underline{r}_2, \underline{r}_3, \dots, \underline{r}_N) \times (1 + \frac{1}{2} r_{12}) \\ &+ \underline{r}_{12} \cdot \underline{c}(\underline{r}_1, \underline{r}_3, \dots, \underline{r}_N) + O(r_{12}^2). \end{aligned} \quad (2.3.2a)$$

The condition (2.3.1a) is satisfied for any nucleus, nuclear charge Z_α , at the origin of the coordinate system. The vector \underline{a} is not determined by the Coulomb singularity but has magnitude depending on the coordinates of the non-coalescing particles and direction parallel to the electric field produced by these particles.⁵² Bingel⁴⁸ also found cusp conditions for the general first order density matrix including

spin, extending Steiner's derivation to include the spin density cusp.

$$\left(\frac{\partial \rho^s}{\partial r}\right)_{r=0} = -2Z \rho^s(0) \quad (2.3.4)$$

Note that the spherical averaging operator needed to express the differential cusp conditions (2.2.1) and (2.3.2) precludes any possibility of obtaining coalescence conditions from these expressions that are not trivial in nature.

Cusp conditions for the special cases of the helium atom and hydrogen molecule have been found and discussed by Roothaan and coworkers.^{49, 50}

Their method was to explicitly consider the ratio,

$H\Psi/\Psi$, for the exact (spinless) wave function.

Among the necessary relations needed to keep this ratio constant are conditions on Ψ similar to those of Kato.* Higher order Coulomb singularities (coalescence of more than two particles) may be examined this way. For more complicated cases, however, this approach becomes very involved. Pack and Byers Brown² were the first to derive rigorously equations similar to (2.3.1a) and (2.3.2a)

* The conditions of Roothaan et al appear the same as Kato's, but a different set of independent variables has been used.

allowing non-trivial coalescence conditions as well as cusp conditions to be found. They also removed the heavy-nucleus approximation. A brief outline of their instructive method is presented here:

The general N-particle Schrödinger equation using the Hamiltonian (2.2.1) was solved in the region of coalescence of two particles (labelled '1' and '2' for convenience)--that is, in the manifold of points $r_{12} \leq \epsilon$, $r_{ij} \gg \epsilon$ for all $r_{ij} \neq r_{12}$ and ϵ , some small positive constant. Transforming the space-fixed position coordinates \underline{r}_1 , \underline{r}_2 to the center of mass and relative coordinates

$$\underline{r}_{12} = \underline{r}_1 - \underline{r}_2 \quad \text{and} \quad \underline{S}_{12} = \frac{m_1 \underline{r}_1 + m_2 \underline{r}_2}{m_1 + m_2}$$

of the two particles, allowed the Schrödinger equation to be rewritten in the vicinity of the coalescence as

$$(H-E)\psi = \left[\frac{Z_1 Z_2}{r_{12}} - \frac{1}{2\mu_{12}} \nabla_{12}^2 + \mathcal{O}(r_{12}^0) \right] \psi = 0 \quad (2.3.5)$$

∇_{12}^2 is the Laplacian operator for the variable \underline{r}_{12} , μ_{12} is the reduced mass, Z_1, Z_2 the charges of the particles, and $\mathcal{O}(r_{12}^0)$ contains all other terms of the Hamiltonian of order equal to or greater than

zero in r_{12} . As $r_{12} \rightarrow 0$, $\mathcal{O}(r_{12}^0) \rightarrow \text{constant}$.

The general bounded solution of (2.3.5) has form

$$\psi = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} r^{\ell} f_{\ell m}(r) Y_{\ell m}(\theta, \phi) \quad (2.3.6)$$

where $\underline{r}_{12} = (r, \theta, \phi)$ and the $Y_{\ell m}$'s are spherical harmonics. For electron-nucleus coalescence, with the nucleus at the origin, \underline{r}_{12} becomes the radius vector \underline{r}_1 of the electron. Substituting (2.3.6) into the differential equation (2.3.5), expanding as a power series in r ,

$$f_{\ell m}(r) = \sum_{k=0}^{\infty} f_{\ell m}^{(k)} r^k \quad (2.3.7)$$

and solving, Pack and Byers Brown found a unique solution, true for $r_{12} \leq \epsilon$,

$$\begin{aligned} \psi = r_{12}^{\lambda} \left\{ \sum_{m=-\lambda}^{+\lambda} f_{\lambda m}^{(0)} Y_{\lambda m}(\theta, \phi) \left[1 + \frac{\gamma}{\lambda+1} r_{12} \right] \right. \\ \left. + r_{12} \sum_{m=-\lambda-1}^{+\lambda+1} f_{\lambda+1, m}^{(0)} Y_{\lambda+1, m}(\theta, \phi) + \mathcal{O}(r_{12}^2) \right\} \end{aligned} \quad (2.3.8)$$

where $\gamma = Z_1 Z_2 / \mu_{12}$.

They defined λ , a parameter related to the nodal structure of the system,* to be the smallest value

* The physical meaning of λ as defined here is lost when the system does not have spherical symmetry about the coalescence. Examples are electron-electron coalescence in atoms, or any type of coalescence in molecules.

of ℓ for which $f_{\ell m}^{(0)} \neq 0$ at the coalescence of the two particles. The equivalent differential form of equation (2.3.8) is ⁵³

$$\left(\frac{\partial \frac{1}{r_{12}^\lambda} \widehat{\Phi}}{\partial r_{12}} \right)_{r_{12}=0} = \frac{\gamma}{1+\lambda} \left(\frac{1}{r_{12}^\lambda} \widehat{\Phi} \right)_{r_{12}=0} \quad (2.3.8a)$$

where the angular average operator, $\widehat{}$, is modified to $\sum_{m=-\lambda}^{+\lambda} \int d\Omega Y_{\lambda m}^*(\theta, \phi)$. This equation gives non-trivial coalescence conditions for the case of a node at coalescence in contrast to earlier approaches. For the (usual) nodeless case λ is zero and Kato's cusp conditions can be recovered as

$$\left(\frac{\partial \widehat{\Phi}}{\partial r_{12}} \right)_{r_{12}=0} = \gamma \widehat{\Phi}_{r_{12}=0}.$$

γ is 1/2 for electron-electron coalescence and

$\gamma = -Z\mu$ for electron-nucleus coalescence--the same value that Kato found, but with a mass correction to the heavy-nucleus approximation.* Note again that all exact spinless wave functions** must have an expansion like (2.3.8) around a Coulomb singularity.

* $\mu = 1$ if mass corrected atomic units are used. See Appendix A.

** Matsen's 'spinless' wave functions are not really spinless. Spin is represented implicitly by applying appropriate permutations of the symmetric group to a spatial solution of the Schrödinger equation. See [16] for further information.

But a spinless wave function is not realistic. Any physically acceptable, quantum-mechanical wave function must contain spin coordinates for its particles. Let us restrict the discussion now to the specific case of N-electron atomic and molecular wave functions. In the Born-Oppenheimer, or heavy-nucleus, approximation the nuclear coordinates do not appear explicitly and only the electronic coordinates need be considered.* (Also the Pauli principle for a system of identical fermions must be obeyed leading to a wave function antisymmetric with respect to the interchange of any two sets of electronic coordinates). In the nonrelativistic approximation both the total-spin operator and an arbitrary spin-component operator commute with the Hamiltonian.

$$[\mathcal{S}^2, H] = [\mathcal{S}_z, H] = 0 \quad (2.3.9)$$

Thus it is desirable that a wave function with spin, $\Phi_{S,M}$, should have sharp total (electronic) spin and a sharp spin component:

$$\begin{aligned} \mathcal{S}^2 \Phi_{S,M} &= S(S+1) \Phi_{S,M} \\ \mathcal{S}_z \Phi_{S,M} &= M \Phi_{S,M} \end{aligned} \quad (2.3.10)$$

*The effects of nuclear spins on the wave function can be included, if necessary, as perturbations.

where $\bar{\Phi}_{S,M} = \bar{\Phi}(\underline{r}_1 s_1, \underline{r}_2 s_2, \dots, \underline{r}_N s_N)$ is a function of space and spin coordinates, \underline{r}_i and s_i , of each electron. Any wave function containing spin can be expanded^{54, 55}

$$\bar{\Phi}_{S,M} = \sum_K \psi_K(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) \Theta_{S,M;K}(s_1, s_2, \dots, s_N). \quad (2.3.11)$$

Here $\bar{\Phi}_{S,M}$ is not normalized. The spin functions $\{\Theta_{S,M;K}\}$ constitute the complete set of linearly independent spin functions for N electrons. They are eigenfunctions of \mathcal{S}^2 and \mathcal{S}_Z having eigenvalues $S(S+1)$ and M respectively. The functions $\{\psi_K\}$ are formed by symmetric group operations on some spatial solution of the Schrödinger equation and are all degenerate energy eigenfunctions. Since an exact spatial solution satisfies the coalescence conditions (2.3.8) each ψ_K must also, necessitating the satisfaction of (2.3.8) by an (exact) spin containing function, $\bar{\Phi}_{S,M}$. And as spherically averaging does not affect the argument, the differential cusp conditions of Kato (2.3.1), (2.3.2) also apply.

These preceding approaches all have the same general limitations:

1. They only treat two particle coalescence. Higher order singularities, when $r_{ij} \rightarrow 0$

for several i, j , are assumed not to occur. Thus the behaviour of exact wave functions at Coulomb singularities has been investigated for a limited number of points in the manifold

$$\{r_{ij} = 0 ; i, j = 1, N ; i \neq j\}.$$

2. They really treat only the spherically symmetric part of the cusp. A spherical average over the wave function in equations (2.3.1a), (2.3.2a), (2.3.8) must be taken if relationships involving completely determined quantities are desired. The angular dependence of the Coulomb cusp arises from the other (N-2) particles.^{2, 52}

In a physical sense these limitations are not severe. The value of the approaches is that necessary conditions for the behaviour of exact wave functions (with spin) at the most important Coulomb singularities have been derived.

2.4 Cusp calculation methods for approximate wave functions *

* Observe the following distinctions to avoid later confusion. Cusp and coalescence conditions given by equations (2.3.1), (2.3.2), (2.3.8) are the ones mentioned and applied in this thesis. An exact wave function necessarily satisfies these conditions, although they are not the only ones. Approximate wave functions can satisfy them also in a necessary and/or sufficient way. These aspects of cusp condition applications will be discussed more fully later in the text.

Wave functions (with their derivatives) obtained by approximate methods do not necessarily have the same types of discontinuities as the corresponding exact functions. If one is striving to copy an exact function, as is usually the case, the approximation could give better point properties if it has the correct behaviour at the singular points. Pluvina⁵⁶ was among the first to apply this reasoning; Kato⁴⁷ was the first to provide a general tool^{*} for describing Coulomb singularities. In this light it is of general interest to analyse the importance of the cusp. How might the proper cusp be important for approximate wave functions? To answer this look at its effect on expectation values. First, the energy.

The electron-electron cusp seems, at first glance, to be directly related to the correlation problem. A proper description of correlation phenomena surely involves the behaviour of the wave function at electron coalescence when two electrons approach the same point in space. Correlated wave functions (containing interelectronic coordinates, r_{ij} , explicitly) converge more rapidly than configuration interaction (CI) expansions without r_{ij} .^{35,57} The difference could

* The absence of a treatment for the higher order singularities should not be too serious [49]. Three body effects appear to be much less important than two body interactions in defining atomic and molecular properties. See, for example reference [5].

be that correlated functions can easily represent exact electron cusps. CI functions for helium with a finite number of terms cannot possibly⁵⁷ since the occurrence of only even powers of r_{ij} in any expansion necessitates $\left(\frac{\partial \Phi_{CI}}{\partial r_{ij}}\right)_{r_{ij}=0} = 0$. (Compare with (2.3.2)). Analyses by Gilbert⁵⁸ and Gimarc, Cooney and Parr,* however, subscribe that adequate description of the Coulomb hole contributes more to correlation energy than does proper cusp behaviour. The cusp region lies inside the energy-important part of the Coulomb hole. Since electron-nucleus contribution to correlation energy is negligible** it would seem that the accuracy of cusps, both electron-electron and electron-nucleus has little to do with the accuracy of energy.

There remains the question with respect to other expectation values. Recall that there is little connection between the accuracy of approximate energy and accuracy of different, approximate properties. Consequently the conclusions reached in the previous paragraph for energy may not be valid for other observables. Reiterating section 1.2, the object of this thesis will be to examine the relationship of the cusp to certain properties--the electron and spin densities

* Quoted by Gimarc and Parr [57] .

** This conclusion of Coulson and Neilson for the case of helium was quoted by Gilbert [58] .

at the nucleus. Previous work done on this specific problem^{59, 60} will be reviewed in a later section.

The next step is to decide how to evaluate cusps for approximate wave functions. Obviously if a function satisfies equations (2.3.1), (2.3.2) or (2.3.8) it has a proper cusp, but this approach is not practical for almost all wave functions, due to the tediousness of the algebra, nor does it give an estimate of the closeness of the cusp to the correct value (δ). Easier methods exist.

The electron-nucleus cusp evaluation for self-consistent field (SCF) orbitals is well documented.^{28,53} (However the remarks concerning electron-electron cusps in CI functions made earlier in this section also apply to SCF functions; it is difficult for a wave function without explicit r_{ij} correlation to have the correct electron-electron cusp). An exact SCF orbital has the general form

$$\varphi_{nlm}(r, \theta, \phi) = r^l f_{nl}(r) Y_{lm}(\theta, \phi) . \quad (2.4.1)$$

n , l , m are the usual orbital quantum numbers; $\{Y_{lm}\}$ are the spherical harmonics. To satisfy the general coalescence conditions (2.3.8a) for electron-nucleus coalescence it is sufficient that the radial

part of φ_{nlm} , $r^\ell f_{nl}(r)$, obey

$$(\ell+1) \left(\frac{\partial f_{nl}}{\partial r} \right)_{r=0} = -Z f_{nl}(0) . \quad (2.4.2)$$

Numerical solutions of the Hartree-Fock (HF) equations have this condition built into them automatically and consequently should have good cusp values. One indication of convergence of the non-exact, analytical HF solutions is the closeness of the ratio

$$\frac{(\ell+1)}{f_{nl}(0)} \left(\frac{\partial f_{nl}}{\partial r} \right)_{r=0} \quad (2.4.2a)$$

to $\gamma = -Z$. Roothaan, Sachs and Weiss²⁸ have mentioned this as an accuracy test of their HF wave functions in the region $r \rightarrow 0$. Clementi⁶¹ has evaluated the ratio for analytical HF orbitals of helium through argon.

Another method for cusp evaluation is due to Chong.⁵³ He changed the form of the coalescence conditions (2.3.8) to relationships between expectation values of SCF orbitals, called integral coalescence conditions. If an SCF orbital, $\varphi_{nlm}(r, \theta, \phi)$, has a correct cusp the radial function $f_{nl}(r)$, (see (2.4.1)), must necessarily satisfy

$$\int_0^\infty dr f_{nl}(r) \delta(r) \left(\frac{Z}{\ell+1} + \frac{\partial}{\partial r} \right) f_{nl}(r) = 0 \quad (2.4.3)$$

The formula $\delta(r) = \frac{\delta(r)}{4\pi r^2}$ has been used here, correct for the spherically symmetric radial function. $\delta(r)$ is the Dirac delta function. Equation (2.4.3) can be extended easily to include the full orbital expression. The spin dependence of SCF orbitals leads to no problems; arguments presented earlier can immediately permit equations (2.4.2) and (2.4.3) to be applied to any SCF spin orbital. In Dirac notation, now, the integral coalescence conditions* for SCF spin orbitals appear like

$$\langle \varphi_{n\ell m}(r, \theta, \phi, s) | \frac{\delta(r)}{r^{\ell+2}} \left(\frac{z}{\ell+1} + \frac{\partial}{\partial r} \right) \frac{1}{r^{\ell}} | \varphi_{n\ell m}(r, \theta, \phi, s) \rangle \quad (2.4.4)$$

$$= 0$$

The deviation from zero of this integral will give an estimate of how close the one-electron SCF orbital $\varphi_{n\ell m}$ comes to having the proper cusp behaviour at the nucleus.

CI wave functions need a different approach. The ratio, (2.4.2a), using differential coalescence conditions may be all right for checking the cusp of SCF orbitals, but it cannot be applied to many-electron CI functions. Because CI functions do not have the

* For the case of atoms, not molecules, equation (2.4.3) contains a 'pseudo-integration' which only involves taking a limit. Chong's integral conditions (2.4.4) are thus necessary and sufficient for atoms.

simple independent particle interpretation of SCF wave functions the integral coalescence conditions (2.4.4) cannot be used directly either. Chong⁶² has been able to find coalescence conditions for CI functions corresponding to (2.4.4) by generalizing the cusp relations of Steiner (2.3.3) for electron density and of Bingel (2.3.4) for both electron and spin density. He obtained equations for integral spin, and integral electron coalescence conditions which can be written compactly as

$$\langle \Phi_{s,m} | \mathcal{G}_\lambda^a | \Phi_{s,m} \rangle = \frac{\gamma}{1+\lambda} \langle \Phi_{s,m} | \mathcal{Z}_\lambda^a | \Phi_{s,m} \rangle. \quad (2.4.5)$$

$a = s$ or e designates the spin or electron conditions respectively. γ, λ have the same meaning as in (2.3.8). $\mathcal{G}_\lambda^a, \mathcal{Z}_\lambda^a$ are the one-electron gradient and density operators evaluated at the nucleus.

$$\mathcal{G}_\lambda^e = \sum_{i=1}^N \frac{1}{r_i^{\lambda+2}} \delta(r_i) \left(\frac{\partial}{\partial r_i} \right) \frac{1}{r_i^\lambda} \quad (2.4.6)$$

$$\mathcal{Z}_\lambda^e = \sum_{i=1}^N \frac{1}{r_i^{\lambda+2}} \delta(r_i) \frac{1}{r_i^\lambda}$$

$$\mathcal{G}_\lambda^s = \sum_{i=1}^N \frac{1}{r_i^{\lambda+2}} \delta(r_i) \left(\frac{\partial}{\partial r_i} \right) \frac{1}{r_i^\lambda} \mathcal{S}_{z_i} \quad (2.4.7)$$

$$\mathcal{Z}_\lambda^s = \sum_{i=1}^N \frac{1}{r_i^{\lambda+2}} \delta(r_i) \frac{1}{r_i^\lambda} \mathcal{S}_{z_i}$$

$\delta(r)$ is the Dirac delta function. Note that for singlet spin states, $\langle \mathcal{S}^2 \rangle = 0$ and the spin coalescence conditions become trivial. For the nodeless case, $\lambda = 0$, $\mathcal{Z}_\lambda^{s,e}$ are the usual density operators, and integral cusp conditions are expressed. Spin density at the nucleus is given by

$$Q^s(0) = \frac{\langle \frac{1}{5} \mathcal{Z}_{\lambda=0}^s \rangle}{4\pi} \quad (2.4.8)$$

and likewise electron density is

$$Q^e(0) = \frac{\langle \mathcal{Z}_{\lambda=0}^e \rangle}{4\pi} \quad (2.4.9)$$

The expressions (2.4.5) are necessary relations for exact wave functions but they are extremely useful in cusp evaluation for any approximate function. Here, as before, the correctness of the cusp is indicated by the values of the integrals in (2.4.5) for the wave function being examined. The value of the approximate cusp,

$$\Gamma^a = (\lambda+1) \frac{\langle \Psi | \mathcal{G}_\lambda^a | \Psi \rangle}{\langle \Psi | \mathcal{Z}_\lambda^a | \Psi \rangle}, \quad a = e, s, \quad (2.4.10)$$

is to be compared with that of the exact cusp

$$\gamma = -Z. \quad (2.4.11)$$

The approach in this work is to force trial wave functions, in various ways, to have

$$\int^a = \gamma \quad (2.4.12)$$

Evidence that this procedure is expected to lead to improved properties is presented in the next section.

2.5 Use of cusp and coalescence conditions for improvement of approximate wave functions

Touched upon in the introduction was the fact that expectation values of point properties are rather special compared with the usual type of observable. They depend on the value of a wave function at a single point and are not averaged out over the space surrounding the system. Thus a wave function that might be quite good when considered throughout space could, indeed, be exceptionally poor at or near certain points. For few examples is this observation more true than the spin density at the nucleus. (See Table I). Any improvement of the approximate function towards the exact in the nuclear region should hopefully improve such point properties as the electron and spin densities there. Naturally other factors--correlation and core polarization for examples--also influence the wave function and these may override any improvement,

at the cusp. But surely a wave function should have the correct behaviour at a point of non-analyticity, and surely theoretical conditions like the cusp relations are just as valid as minimum energy for determining the function.

This reasoning--that a function with a correct cusp is a better function--has been seized on by many workers. Roothaan, Weiss and Kolos^{49,50} constructed correlated functions for helium and the hydrogen molecule which have the correct electron-electron and electron-nucleus cusps. Conroy⁶³ has used special cusp-satisfying bases in his unique calculations and Parr, Weare and Weber⁶⁴ have investigated cusp-satisfying Hulthén orbitals. Kelly and Roothaan⁶⁵ presented a treatment that shows how to choose a Slater-type orbital (STO) basis so that atomic SCF orbitals will satisfy the coalescence conditions at the nucleus; merely use the set of STO's

$$1s, 3s, 4s, \dots; 2p, 4p, 5p, \dots; 3d, 5d, 6d, \dots \quad (2.5.1)$$

where the first orbital of any angular symmetry ($\ell = n-1$) has fixed orbital exponent

$$J_n = \frac{Z}{n} \quad , \quad (2.5.2)$$

the members $\{ 2s, 3p, 4d, \dots \}$ are not present, and all other exponents are free to be varied. Any atomic SCF orbital expressed as a linear combination of members from this special set will automatically have the correct behaviour at the nuclear cusp. This choice of basis is becoming quite normal in SCF-type atomic calculations.^{21, 65, 66, 67} Another procedure is available for SCF calculations--a constrained variational approach of Handy, Parr and Weber⁶⁸ based on their elegant constraint procedure ([69] and Appendix C) --but is discussed in Chapter IV. The assumption that a better wave function is obtained is the only apparent rationale behind this flurry of producing cusp-satisfying approximate wave functions.

With a view towards clarifying the question, 'Does a good cusp really mean an intrinsically better wave function?', Chong and Schrader⁶⁰ examined the statistical correlation between electron density and cusp in various helium wave functions ranging from simple SCF to highly correlated ones. They discovered a strong correlation between the error in the nuclear cusp and the error in the electron density at the nucleus. See figure 1. When compared with the low degree of correlation between the error in the cusp and the accuracy of energy, this result becomes important

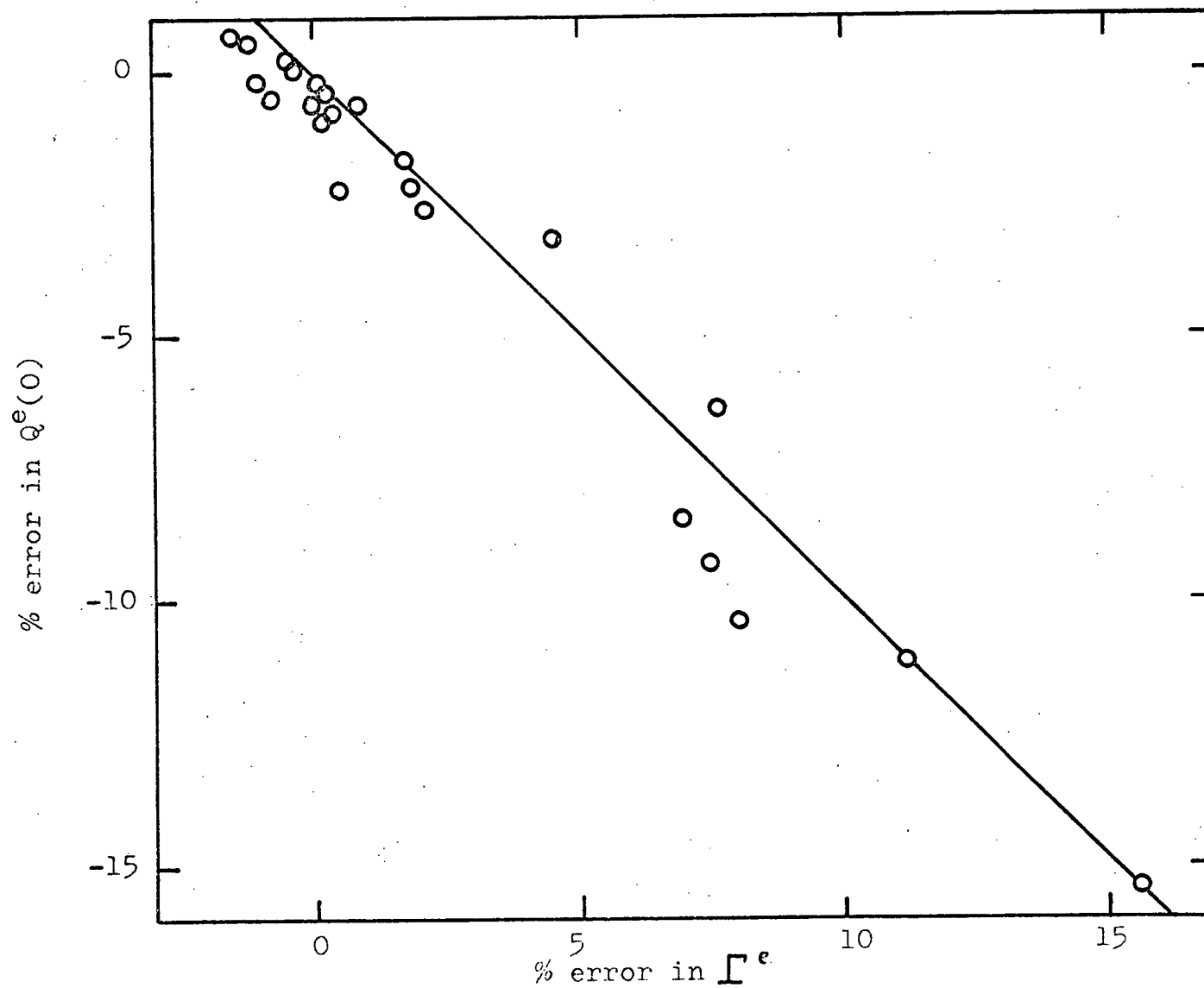


Figure 1. Correlation between error in nuclear cusp and error in $Q^e(0)$ for He wave functions, found by Chong and Schrader.⁶⁰

implying that improvement of the cusp does improve at least the electron density, $Q^e(0)$. A high correlation between the electron-electron cusp and the expectation value $\langle \delta(r_{12}) \rangle$ was also found but here a larger correspondence between the cusp value and the energy exists making a similar conclusion invalid for the point density $\langle \delta(r_{12}) \rangle$.

Having this justification Chong and Yue⁵⁹ applied the theory of linear constraints (Appendix C) to various helium CI (without r_{ij}) functions of 3-8 terms with the idea of forcing simple, easily calculated wave functions to have a good $Q^e(0)$. The conclusions of Chong and Schrader⁶⁰ are qualitatively substantiated in their study. A fairly flexible function was found to be necessary to absorb the effect of the constraint. In the cases tested though, the application of the cusp constraint, $\Gamma^e = \gamma$, (see the text preceding (2.4.12)), while improving $Q^e(0)$, led to a slight over-correction. Unfortunately, errors in the values $\langle r^{-2} \rangle$, $\langle r^{-1} \rangle$ did not decrease upon constraint as might be expected from an improvement of the function near the nucleus. This approach of Chong and Yue with respect to cusp satisfaction, however, is unique and needs further investigation. It will be used in the next chapter on lithium wave functions to check possible improvements in both $Q^e(0)$ and $Q^s(0)$.

CHAPTER III

INTEGRAL CUSP CONSTRAINTS AND APPLICATIONS
TO LITHIUM $2S$ GROUNDSTATE FUNCTIONS3.1 Formation of constraints

The correlation between error in nuclear cusp and error in $Q^e(0)$ for approximate helium wave functions⁶⁰, discussed in Section 2.5, led to the discovery that when a He CI wave function was forced to have a good cusp value, $\Gamma^e = -Z$, its electron density improved⁵⁹, providing the function had enough linear parameters to absorb the effect of constraining. Attempts to substantiate these results for Li $2S$ groundstate wave functions are described in this chapter. Of primary interest though is the additional possibility of correlations between $Q^s(0)$ and Γ^e or Γ^s , since the states of helium examined^{59, 60} have no spin density. Because Γ^e need not equal Γ^s for approximate wave functions, the effect of a double constraint, $\Gamma^e = \Gamma^s = -Z$ is tested. Various off-diagonal 'weighting' constraints are developed and applied as well.

Note the following points:

- (1) Integral cusp constraints are only necessary conditions and the fact that $\Gamma^{e,s} = -Z$ does not mean the function has the correct cusp.
- (2) Since Γ is a ratio, constraining it does not dictate a value for $Q^{e,s}(0)$.
- (3) There is no immediate interest in developing a constraint for the electron-electron cusp.

In constrained variation one wishes to minimize the energy of an approximate wave function subject to a certain number (k) of constraints. The basic procedure is to define constraint operators, \mathcal{G}_i , describing the attributes to be constrained, so that when the constraints are satisfied, $\langle \mathcal{G}_i \rangle = 0$ for each i . The modified variational principle takes the form

$$\langle \delta \psi | \{ H + \sum_{i=1}^k \lambda_i \mathcal{G}_i - E_c \} | \psi \rangle = 0 \quad (3.1.1)$$

where H is the Hamiltonian for the system, E_c is the energy of the constrained eigenfunction and λ_i ,

the Lagrange multipliers, are to be determined. The term single constraint means $K = 1$. Likewise $K = 2$ implies a double constraint. Appendix C contains a summary of methods to solve (3.1.1). Following Chong^{53,62} and Chong and Yue⁵⁹ the constraint operators employed in this work for the nuclear cusp condition have the form

$$G^a = \frac{1}{2} (\rho^a + \rho^{a\dagger}) , \quad a = e, s \quad (3.1.2)$$

where $\rho^a = \mathcal{G}_{\lambda=0}^a - \gamma \mathcal{Z}_{\lambda=0}^a$ and \mathcal{G}, \mathcal{Z} are defined in equations (2.4.7). When such a constraint is imposed, $\langle G \rangle = 0$ implies

$$\Gamma^a = \frac{\langle \mathcal{G}_{\lambda=0}^a \rangle}{\langle \mathcal{Z}_{\lambda=0}^a \rangle} = \gamma = -Z \quad (3.1.3)$$

as desired. The constrained variational solution of (3.1.1) is the eigenvector having the lowest eigenvalue of the matrix representation of the fictitious Hamiltonian

$$h_{\text{fict}} = H + \sum_{i=1}^K \lambda_i G_i \quad (3.1.4)$$

and satisfying $\langle G_i \rangle = 0$. Thus G_i must be Hermitian. The operator \mathcal{Z} is Hermitian but \mathcal{G} is not; hence the form for G in (3.1.2). This is not a unique

choice. A whole hierarchy of Hermitian combinations of \mathcal{L} and \mathcal{L}^\dagger will also lead to (3.1.3), for example. The results obtained from different \mathcal{G} 's are expected to be qualitatively the same.

A diagonal constraint results in the condition

$$\langle \psi | \mathcal{G} | \psi \rangle = 0 \quad (3.1.5)$$

and is best solved using the well-developed methods of Byers Brown, Chong and Rasiel.^{70, 71, 72} An off-diagonal constraint,

$$\langle \phi | \mathcal{G} | \psi \rangle = 0, \quad \phi \neq \psi \quad (3.1.6)$$

where ϕ may be an excited state or even an (almost) arbitrary weighting function, is easily imposed by the recently published method of Weber and Handy.⁶⁹

All wave functions in this work are initially characterized by their free variational form--that is, with no constraint imposed save normalization. The usual Slater-type orbital (STO) one-electron basis, $\{\chi_i\}$,

$$\chi_{n\ell m}(r, \theta, \phi) = N_n r^{n-1} e^{-sr} Y_{\ell m}(\theta, \phi), \quad (3.1.7)$$

$$N_n = \sqrt{\frac{(2s)^{2n+1}}{(2n)!}}$$

is always employed. The orbital exponents, ζ , if varied, are successively optimized by parabolic interpolation to minimum energy.³⁰ One iteration cycle is completed when all exponents have been optimized once. Usually two or three cycles will ensure a minimized energy providing the initial estimates of the exponents are reasonable. Since the spin function Θ_2 in (2.1.8) does not contribute significantly towards energy, it is not included until after exponent optimization. Terms containing Θ_2 will be designated Θ_2 -type terms, or triplet core spin terms.

To solve (3.1.1) a transformation of all matrices from configurational space to the basis of free variational eigenfunctions $\{\xi_i\}$ is advantageous for two reasons:

- (1) An orthonormal basis simplifies calculations.
- (2) This transformation leads to conceptual advantages--a constrained function appears as the free variational groundstate eigenfunction with small 'corrective' terms.

$$\psi_c = \xi_1 + \sum_{i=2} a_i \xi_i, \quad (3.1.8)$$

$$|a_i| \ll 1$$

The severity of the imposed constraint can be estimated by either the rate of convergence towards the correct constrained function, or the energy sacrifice

$$\Delta E = E_c - E_{\text{free variational}} .$$

3.2 Exploratory calculations

It was hoped at the start of this work that reasonable spin densities could be obtained merely by constraining any simple function to satisfy the nuclear cusp conditions. Consequently a rather naive initial approach was taken. The first wave functions examined did not lead to unambiguous conclusions. They did, however, illustrate the computational difficulties encountered and indicated a more refined approach to be described in the next (3.3) section.

Two types of functions were developed for this initial study. The first type was comprised of a series of functions having 4-8 terms and partially (not completely) optimized orbital exponents. The 7 and 8 term functions, containing triplet core spin terms and some p-type angular correlation, are actually quite good in spite of their simplicity but are not flexible enough for a meaningful study on the effect of constraining. The second type, a series of 10-15

terms, with an increasing number of triplet core spin terms, and with p-type correlation, had orbital exponents transplanted from the Li CI functions of Weiss.³⁵ This group is poor indeed with respect to energy, but slightly more flexible than the first series.

Several different attempts to solve (3.1.1) for single constraints are now discussed with Ψ_7 , the seven term function from the first group, as an example. It became necessary to investigate this aspect when the perturbation approach⁷⁰ failed to give an initial value to λ , the Lagrange multiplier, for several functions. Series divergences, exponent overflows, etc., are characteristic results of attempting to constrain inflexible functions using a perturbation-type approach. Since prediction of which functions cause difficulties is uncertain, finding a foolproof method of solving (3.1.1) is helpful.

The free variational description of Ψ_7 , with its properties free and constrained is listed in Table II. Although $Q^e(0)$ shows a 2% improvement, the energy sacrifice, ΔE , for the constraint $\Gamma^e = \gamma$ is high; the strange value of $Q^s(0)$ also indicates the severity of this constraint. Contrast with the corresponding case $\Gamma^s = \gamma$. The function, Ψ_7 , is atypical but it provides a good test case. These cusp constraints

provide the first example of failure of the perturbation approach; the desired behaviour is illustrated in Table III by a flexible (for a 2 electron system) 7 term helium wave function, ϕ_7 , of Yue and Chong⁵⁹ and compared with the behaviour of Ψ_7 (Li).

Only the parametrization approach remains. Here fictitious wave functions are calculated from (3.1.1) for different values of λ until, for some optimum, λ_{opt} , a root of

$$C(\lambda) = \langle \Psi | \mathcal{C} | \Psi \rangle = \langle \mathcal{C} \rangle = 0 \quad (3.2.1)$$

where $\Psi(\lambda)$ is found from (3.1.1). At $\lambda = \lambda_{\text{opt}}$

$$C(\lambda_{\text{opt}}) \equiv 0 \equiv \langle \Psi_c | \mathcal{C} | \Psi_c \rangle. \quad (3.2.2)$$

The problem is that unless one approximately knows λ_{opt} , it can be difficult to locate. To understand better what is involved in solving (3.2.1) $C(\lambda)$ was plotted against λ for several functions. The curve for Ψ_7 , $\mathcal{C} = \mathcal{C}^e$, is shown in figure 2(A).

This 'titration' curve is typical for any constraint as can easily be ascertained by considering $C(\lambda)$ for $\lambda \gg 0$ and $\lambda \ll 0$. When $\lambda \gg 0$, $E_{\text{fict}} \approx \lambda \mathcal{C}$ and $\Psi(\lambda)$ is the eigenfunction having the lowest eigenvalue $E_{\text{fict}}(\lambda) \approx \lambda C_1$, C_1 being the lowest

Table II. Description and Properties of Ψ_7 .

STO basis:	χ_{1s}	χ_{1s}'	χ_{1s}''	χ_{2s}	χ_{2p}	χ_{3s}
Exponent:	3.298	2.068	0.433	0.639	3.992	1.090
Configurations:	$\chi_{1s} \chi_{1s}' \chi_{1s}'' \theta_1$, $\chi_{1s} \chi_{1s}' \chi_{1s}'' \theta_2$, $\chi_{1s} \chi_{1s}' \chi_{2s} \theta_1$, $\chi_{1s} \chi_{1s}' \chi_{2s} \theta_2$, $(\chi_{2p})^2 \chi_{2s} \theta_1$, $(\chi_{2p})^2 \chi_{1s}'' \theta_1$, $\chi_{1s} \chi_{1s}' \chi_{3s} \theta_1$					
Linear coefficients: for the groundstate	-0.108016 , 0.004854 , 0.540761 , -0.004979 , -0.030853 , $+0.007831$, $+0.092132$					
Prop- erties:	Free Variational	Single Constraints				
		$\Gamma^e = \gamma$		$\Gamma^s = \gamma$		
$-E$	7.466022	7.340290		7.466004		
ΔE	---	0.125732		0.000018		
λ	---	$0.80683335 \times 10^{-2}$		$-0.99947345 \times 10^{-4}$		
$Q^s(0)$	0.22702	2.40254		0.18609		
$Q^e(0)$	13.45413	13.92203		13.45457		
Γ^e	-2.89513	-3.00000		-2.89500		
Γ^s	-3.12497	-3.81128		-3.00000		

Table III. Term-wise comparison of convergence for
 perturbation expansion of ΔE , the energy
 sacrifice from the $\Gamma^e = \delta$ constraint

	$\phi_7[59]$ for helium	\mathcal{V} for lithium
Correct λ	1.021239×10^{-3}	0.806833×10^{-2}
Order of contribution		
$E^{(1)}$	3.749950×10^{-5}	1.43056×10^{-1}
$E^{(2)}$	-1.855863×10^{-5}	-2.56846×10^{-3}
$E^{(3)}$	-1.26147×10^{-7}	-1.91646×10^{-3}
$E^{(4)}$	-9.4319×10^{-10}	-1.68385×10^{-3}
$E^{(5)}$	-6.7909×10^{-12}	-1.47305×10^{-3}
$E^{(6)}$	-4.699×10^{-14}	-1.28706×10^{-3}
$E^{(7)}$	-3.109×10^{-16}	-1.12355×10^{-3}
Sum of contributions to 7 th order	$\sum_{n=1}^7 E^{(n)} \lambda^n = 1.881378 \times 10^{-5}$	$\sum_{n=1}^7 E^{(n)} \lambda^n = 0.13300$
Correct ΔE	1.881378×10^{-5}	0.12573

eigenvalue of \mathcal{C} . Thus $\langle \mathcal{C} \rangle \approx \frac{\langle \Psi(\lambda) | \mathcal{C} | \Psi(\lambda) \rangle}{\langle \Psi(\lambda) | \Psi(\lambda) \rangle} = c_1$.

When $\lambda \ll 0$, $\mathcal{H}_{fict} \approx -|\lambda| \mathcal{C}$ and $E_{fict}(\lambda) \approx -|\lambda| c_n$

where c_n is the highest eigenvalue of \mathcal{C} . Thus

$$\langle \mathcal{C} \rangle \approx \frac{\langle \Psi(\lambda) | \mathcal{C} | \Psi(\lambda) \rangle}{\langle \Psi(\lambda) | \Psi(\lambda) \rangle} = c_n.$$

These relations are compactly described

$$C(+\infty) = c_1, \quad C(-\infty) = c_n, \quad (3.2.3)$$

and are illustrated in figure 2(A) also. The feature which appears to cause difficulty is the extreme slope (> 500) of $C(\lambda)$ as it crosses the λ axis at λ_{opt} .

Great sensitivity of $\langle \mathcal{C} \rangle$ to λ might be anticipated

from the nature of the curve, and is found; λ_{opt}

must be computed to 5-8 figures to ensure a small

value ($< 10^{-3}$) for $\langle \mathcal{C} \rangle$. The constrained energy is

not nearly so sensitive. The fictitious energy $E_{fict}(\lambda)$,

is the lowest eigenvalue of the fictitious Hamiltonian

$$\mathcal{H}_{fict} = H + \lambda \mathcal{C}; \quad (3.2.4)$$

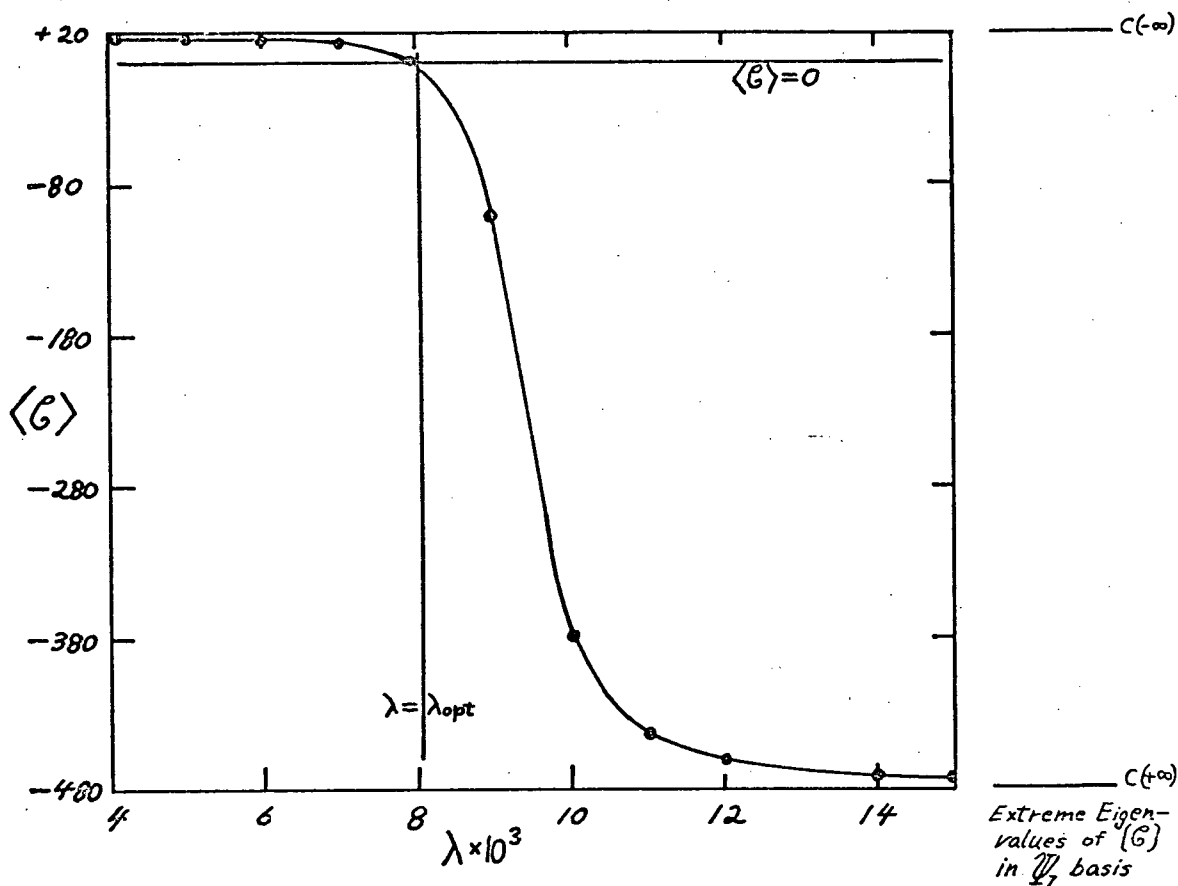
when $\lambda = \lambda_{opt}$

$$E_{fict}(\lambda_{opt}) = \langle H + \lambda \mathcal{C} \rangle = \langle H \rangle = E_{true}(\lambda_{opt}) \quad (3.2.5)$$

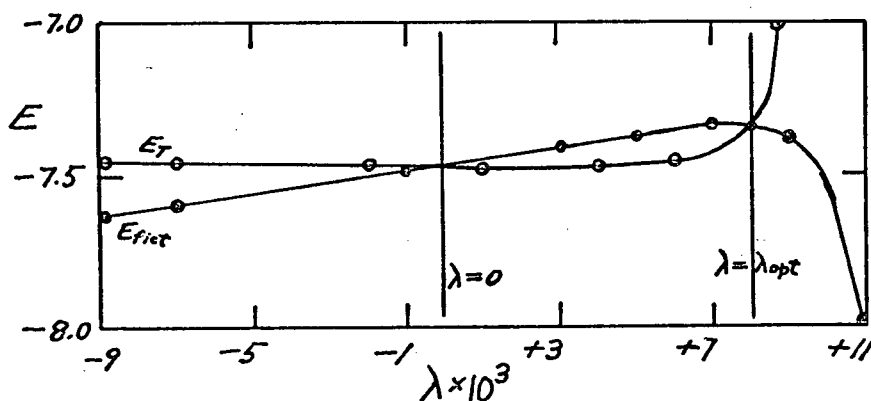
where E_{true} is the real energy of the constrained func-

tion. $E_{fict}(\lambda)$ and $E_{true}(\lambda)$ are plotted in figure 2(B)

Figure 2. (A) Graph of $\langle G \rangle$ versus λ for the ground state of Ψ_7 in electronic cusp constraint



(B) Graphs of fictitious energy, $E_{fict} = \langle H + \lambda G \rangle$, and true energy, $E_T = \langle H \rangle$ versus λ for ground state of Ψ_7 in electronic cusp constraint.



for the $\Gamma^e = \gamma$ constraint of \mathcal{V}_γ . Because $C(\lambda)$ is a monotonically decreasing curve (easily proved from results of the perturbation approach in Appendix C) it has but one zero, $\lambda = \lambda_{\text{opt}}$, at which point $E_{\text{true}} = E_{\text{fict}}$, defining the constrained ground state. As seen in figure 2(B), $E_{\text{true}} = E_{\text{fict}}$ when $\lambda = 0$ as well.

An analytical approximation of the 'titration' curve could provide what the perturbation approach failed to--the initial estimate of λ_{opt} . Several functional forms were investigated, utilizing as readily obtainable parameters the extreme eigenvalues of the matrix representation of \mathcal{G} , the free variational expectation value $\langle \mathcal{G} \rangle_{\lambda=0}$ and various derivatives of $C(\lambda)$ at $\lambda = 0$. They are described here for the possible use and enjoyment of others doing constrained variations.

The basic parameters are defined:

$$\left. \begin{aligned} \alpha &= C(+\infty) \\ \beta &= C(-\infty) \end{aligned} \right\} \text{see (3.2.3)}$$

$$C = C(0)$$

$$B = C'(0) = 2E^{(2)}$$

$$D = C''(0) = 6E^{(3)}$$

where $C^k(0) = \left(\frac{\partial^k C}{\partial \lambda^k} \right)_{\lambda=0}$, and $E^{(k)}$ is the k^{th} order perturbation energy associated with the fictitious Hamiltonian (3.2.4).^{*} Define

$$R = (\alpha - \beta)/2 ; \quad M = (\alpha + \beta)/2$$

and the reduced quantities

$$m = \frac{M}{R} ; \quad c = \frac{C}{R} ; \quad b = \frac{-B}{R} ; \quad d = \frac{-D}{R} .$$

Then the general functional form

$$C(\lambda) \approx M - R \tanh k(\lambda - L) ; k, L, \text{ constants} \quad (3.2.6)$$

has a zero at

$$\Lambda_0 = \frac{(1+c-m)(1-c+m)}{2b} \ln \frac{(1+c-m)(1+m)}{(1-c+m)(1-m)} \quad (A_1) = (3.2.7)$$

^{*} If the fictitious energy is expanded in the perturbation series (see the perturbation approach in Appendix C)

$$E_{\text{fict}}(\lambda) = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots = \langle H + \lambda G \rangle ,$$

$$\text{then } C(0) = \left(\frac{\partial E_{\text{fict}}}{\partial \lambda} \right)_{\lambda=0} = E^{(1)}$$

$$C'(0) = \left(\frac{\partial^2 E_{\text{fict}}}{\partial \lambda^2} \right)_{\lambda=0} = 2 E^{(2)}$$

$$C''(0) = \left(\frac{\partial^3 E_{\text{fict}}}{\partial \lambda^3} \right)_{\lambda=0} = 6 E^{(3)} .$$

If the value of the second derivative is used ($C''(0)$ instead of $C'(0)$),

$$A_0 = \pm \sqrt{\frac{c-m}{d[1 + \cosh \ln \frac{1+c-m}{1-c+m}]}} \ln \frac{(1+c-m)(1+m)}{(1-c+m)(1-m)} \quad (A_2)$$

Now redefine R,

$$R = (\alpha - \beta)/\pi$$

Then

$$C(\lambda) \approx M - R \arctan k(\lambda - L) \quad (3.2.8)$$

has a zero at

$$A_0 = \frac{1}{b} \cos(c-m) \frac{\sin c}{\cos m} \quad (B_1) = (3.2.9)$$

If $C''(0)$ is used instead of $C'(0)$

$$A_0 = \pm \sqrt{\frac{\sin 2(c-m)}{d}} \frac{\sin c}{\cos m} \quad (B_2) = (3.2.10)$$

Cubic factors as arguments of the tanh or arctan functions were tried also. The general form for these curves is

$$C(\lambda) \approx M - R \tanh k[(\lambda - L)^3 + a], \quad a, k, L, \text{ constants} \quad (C) = (3.2.11)$$

and

$$C(\lambda) \approx M - R \arctan k[(\lambda-L)^3 + a] \quad (D) = (3.2.12)$$

where R is defined as in (3.2.6) or (3.2.8) for \tanh or \arctan functions respectively. Table IV gives the results obtained from \mathcal{V}_7 for the $\Gamma^e = \gamma$ constraint. The parameters used for each evaluation are given in the 'Parameter' column. An estimate $\lambda_0 \approx \lambda_{\text{opt}}$ should have at least the correct order of magnitude to be helpful. Remember that this illustrative case is pathological; less severe constraint problems ($\Gamma^s = \gamma$ for example) can be solved easily with these methods or any others.

One other exotic application of the parametrization approach was tried. Since the convergence of the perturbation series (see Table III) depends on $|\lambda|$, the coordinate system for a titration curve such as in figure 2 was shifted, making use of the estimates λ_0 just discussed. The transformation can be seen as follows:

$$h_{\text{fict}} = H + \lambda \mathcal{C} = (H + \lambda_0 \mathcal{C}) + \delta \mathcal{C} = H' + \delta \mathcal{C}$$

where δ is a new perturbation parameter. However

Table IV. Analytical parametrizations of $\Gamma^e = \gamma$ constraint on Ψ_7 .

Equation	Parameters employed	Λ_o ^a
A_1	$C(\pm\infty)$, $C(0)$, $C'(0)$,	0.054
A_2	$C(\pm\infty)$, $C(0)$, $C''(0)$	± 0.0221
C	$C(\pm\infty)$, $C(0)$, $C'(0)$, $C''(0)$	0.015
C	$C(\pm\infty)$, $C(0)$, $C'(0)$ ($a=0$)	0.059
C	$C(\pm\infty)$, $C(0)$, $C''(0)$ ($a=0$)	0.025
B_1	$C(\pm\infty)$, $C(0)$, $C'(0)$	0.02
B_2	$C(\pm\infty)$, $C(0)$, $C''(0)$	0.012
D	$C(\pm\infty)$, $C(0)$, $C'(0)$, $C''(0)$	0.010
D	$C(\pm\infty)$, $C(0)$, $C'(0)$ ($a=0$)	0.059
D	$C(\pm\infty)$, $C(0)$, $C''(0)$ ($a=0$)	0.017

^aThe correct value is $\lambda_{opt} = 0.0080683335$.

the new perturbation series did not always converge rapidly enough.

Having discarded more sophisticated approaches of solving (3.1.1) for single cusp constraints by parametrization the method finally settled upon was a combination of regula falsi with half intervals. (Even regula falsi was not sufficient by itself because the steepness of the curve (3.2.1) at λ_{opt} sometimes led to impossibly slow convergences). Chong's fast perturbation-iteration method⁷² was employed for most $\Gamma^s = \gamma$ type constraints since these were usually imposed easily.

From this exploratory study came some preliminary conclusions noted now without further description of wave functions or expectation values. Except for Larsson's results⁶ the profound effect of Θ_2 -type terms on $Q^s(0)$ was not well documented at the time this work was started. It appears that inclusion of these terms improves $Q^s(0)$ only for partially or fully optimized CI functions. (See the excellent value of $Q^s(0)$ for \mathcal{W}_7 in Table II). $\Gamma^e = \gamma$ constraints invariably overcorrected $Q^e(0)$ often leaving a similar error of opposite sign, while $\Gamma^s = \gamma$ constraints yielded poorer spin densities than the free variational values. A paradoxical situation exists. Optimized (with respect

to energy) CI functions having an appreciable percentage of Θ_2 -type terms give good $Q^S(0)$ values, but do not constrain easily, while less accurate, but more flexible wave functions do not give a reliable $Q^S(0)$ in any case. The idea of constrained variation does not appear to work. Optimum CI functions for a many-electron case, however, are unpractical to construct and thus do not provide a good route to accurate $Q^S(0)$ calculations. So a further attempt was made to show $Q^S(0)$ improvement with cusp constraints using methodically constructed CI functions. These functions must be long enough to absorb the constraint, partially optimized with respect to important exponents, and they must contain Θ_2 -type terms.

3.3 Systematic study

CI functions now discussed provide a reasonable description of both core polarization and correlation effects. It should not be too difficult to obtain similar functions capable of giving good spin densities and other properties for at least the first row elements. The main purpose here, again, is to try to find a favourable correlation between cusp constraints and spin densities. The formation of these CI functions proceeded as follows:

A $2s$ function for groundstate lithium was represented as

$$\Phi = \mathcal{A} [\varphi_{1s}(1) \varphi'_{1s}(2) \varphi_{2s}(3) \Theta_1], \quad (3.3.1)$$

\mathcal{A} the antisymmetrization operator, and the φ_i 's, like analytical Hartree-Fock orbitals. These orbitals were linearly expanded in terms of STO's, $\{\chi_i\}$.

$$\varphi_{1s} = a_1 \chi_{1s} + b_1 \chi_{2s}$$

$$\varphi'_{1s} = a_2 \chi'_{1s} + b_2 \chi'_{2s} \quad (3.3.2)$$

$$\varphi_{2s} = a_3 \chi''_{2s} + b_3 \chi''_{3s}$$

The notation is straight forward; STO's with the same orbital angular momentum quantum number (ℓ) and designated with the same prime (') have identical orbital exponents. Φ was expanded as a CI function (with the accompanying products of a_i 's and b_i 's taken as independent linear coefficients) in terms of STO configurations. Thus the key wave function has eight terms

$$\begin{aligned}
\Phi_8 = & \mathcal{A} \left[\{ a_1 (\chi_{1s} \chi_{1s}' \chi_{2s}'') + a_2 (\chi_{1s} \chi_{2s}' \chi_{2s}'') + a_3 (\chi_{2s} \chi_{1s}' \chi_{2s}'') \right. \\
& + a_4 (\chi_{2s} \chi_{2s}' \chi_{2s}'') + a_5 (\chi_{1s} \chi_{1s}' \chi_{3s}'') + a_6 (\chi_{1s} \chi_{2s}' \chi_{3s}'') \\
& \left. + a_7 (\chi_{2s} \chi_{1s}' \chi_{3s}'') + a_8 (\chi_{2s} \chi_{2s}' \chi_{3s}'') \} \Theta_1 \right] \quad (3.3.3)
\end{aligned}$$

Because φ_{1s} is not equal to φ_{1s}' core polarization is built into the wave function. There is a minimum of non-linear parameters to vary and absence of configurations mixing the φ_i 's avoids interference between terms. The three orbital exponents, ζ_s , ζ_s' , ζ_s'' were optimized for the first four terms, (Φ_4). With these values as initial estimates a single optimization cycle for Φ_8 provided the final values of these non-linear parameters. p-type correlation was next included. Three trial additions of two terms each were compared:

$$\Phi_{10} = \{ \Phi_8 \} + \mathcal{A} \left[\{ a_9 (\chi_{2s}'' \chi_{2p} \chi_{2p}) + a_{10} (\chi_{2s}'' \chi_{3p} \chi_{3p}) \} \Theta_1 \right]$$

$$\Phi_{10}' = \{ \Phi_8 \} + \mathcal{A} \left[\{ a_9 (\chi_{1s}''' \chi_{2p} \chi_{2p}) + a_{10} (\chi_{1s}''' \chi_{3p} \chi_{3p}) \} \Theta_1 \right]$$

$$\begin{aligned}
\Phi_{10}'' = & \{ \Phi_8 \} + \mathcal{A} \left[\{ a_9 (\chi_{1s}''' \chi_{2p} \chi_{2p}) \right. \\
& \left. + a_{10} (\chi_{2s}'' \chi_{2p} \chi_{2p}) \} \Theta_1 \right] \quad (3.3.4)
\end{aligned}$$

Here $\{\Phi_8\}$ means the terms in Φ_8 with only the linear coefficients to be recalculated. The additional exponents, S_s''' , S_p , were partially optimized with one cycle in each 10-term function. The simplest,

Φ_{10} , had the lowest energy and the other two were discarded. Next the eight possible triplet core spin terms were added one at a time, in no special order, changing no exponents, to Φ_{10} , yielding a sequence of functions from 10 to 18 terms in length, with 0 to 8

Θ_2 -type terms ($\Phi_{10} \rightarrow \Phi_{18}$). Because the triplet core terms were added somewhat arbitrarily, one other function, Φ_{14a} , was computed, incorporating the four Θ_2 -type terms producing the largest individual fractional energy decreases in the above series. Both single ($\Gamma^e = \gamma$, $\Gamma^s = \gamma$) and double* ($\Gamma^e = \Gamma^s = \gamma$) cusp constraints were applied to each function. Descriptions of Φ_{10} , Φ_{14} and Φ_{18} are found in Table V. Table VI contains their free variational and constrained properties. Similar tables for the complete series are in Appendix E.

First examine the free variational properties (Table VI). Note that Θ_2 -type terms do not contribute significantly to the energy, the total increment,

* Double diagonal constraints are easily imposed by the method of Chong and Benston [73] described in Appendix C, making use of the results for single constraints.

Table V. Descriptions of Φ_{10} , Φ_{14} , Φ_{18} .

STO Basis Orbitals: $\chi_{1s}, \chi_{2s}, \chi_{1s'}, \chi_{2s'}, \chi_{2s''}, \chi_{3s'}, \chi_{2p}, \chi_{3p}$

Orbital Exponents: 3.168, 3.168, 2.840, 2.840, 0.765, 0.765, 4.974, 4.974

Configurations

$$\begin{aligned}
 \Phi_{10} : & \quad 1s1s'2s''\theta_1, \quad 1s2s'2s''\theta_1, \\
 & \quad 2s1s'2s''\theta_1, \quad 2s2s'2s''\theta_1, \\
 & \quad 1s1s'3s''\theta_1, \quad 1s2s'3s''\theta_1, \\
 & \quad 2s1s'3s''\theta_1, \quad 2s2s'3s''\theta_1, \\
 & \quad 2s''(2p)^2\theta_1, \quad 2s''(3p)^2\theta_1 \\
 \Phi_{14} : & \quad \{\Phi_{10}\}^*, 1s1s'2s''\theta_2, \quad 1s2s'2s''\theta_2, \\
 & \quad 2s1s'2s''\theta_2, \quad 2s2s'2s''\theta_2 \\
 \Phi_{18} : & \quad \{\Phi_{14}\}^*, 1s1s'3s''\theta_2, \quad 1s2s'3s''\theta_2, \\
 & \quad 2s1s'3s''\theta_2, \quad 2s2s'3s''\theta_2
 \end{aligned}$$

Free Variational
Coefficients:

$$\begin{aligned}
 \Phi_{10} : & \quad +0.196099; +0.334607; -0.230831; \\
 & \quad +0.024179; +0.161653; +0.229143; \\
 & \quad -0.165463; +0.018404; -0.010172; \\
 & \quad -0.014436. \\
 \Phi_{14} : & \quad +0.195868; +0.337217; -0.230859; \\
 & \quad 0.022274; +0.161696; +0.226320; \\
 & \quad -0.164641; +0.019763; -0.010174; \\
 & \quad -0.014436; -0.583381; +0.052004; \\
 & \quad -0.056793; +0.012474. \\
 \Phi_{18} : & \quad +0.196595; +0.349087; -0.239527; \\
 & \quad +0.021249; +0.160845; +0.215740; \\
 & \quad -0.156697; +0.020425; -0.010176; \\
 & \quad -0.014440; -2.035945; 0.181852; \\
 & \quad -0.196107; +0.036096; 1.605262; \\
 & \quad -0.143961; 0.153566; -0.026107.
 \end{aligned}$$

* See the text following (3.3.4) for the meaning of the notation $\{\Phi_i\}$.

Table VI. Free variational and constrained properties of Φ_{10} , Φ_{14} , Φ_{18} (defined in Table V)

Function	Constraint	-Energy	$Q^S(0)$	$Q^e(0)$	Γ^e	Γ^S	ΔE	λ
Φ_{10}	None	7.467389	0.2677	13.7522	-2.9732	-3.2795	---	0.0
	$\Gamma^e = \gamma$	7.467254	0.2753	13.9191	-3.0000	-3.2973	0.000135	$+0.579772 \times 10^{-4}$
	$\Gamma^S = \gamma$	7.465334	0.1715	13.5519	-2.9447	-3.0000	0.002055	-0.521667×10^{-2}
	$\Gamma^e = \Gamma^S = \gamma$	7.464736	0.1686	13.8901	-3.0000	-3.0000	0.002653	$\lambda^e = +0.125277 \times 10^{-3}$ $\lambda^S = -0.585347 \times 10^{-2}$
Φ_{14}	None	7.467429	0.2136	13.7500	-2.9728	-2.9790	---	0.0
	$\Gamma^e = \gamma$	7.467291	0.2153	13.9192	-3.0000	-2.9870	0.000138	0.582329×10^{-4}
	$\Gamma^S = \gamma$	7.467429	0.2150	13.7500	-2.9728	-3.0000	$\sim 10^{-8}$	0.891716×10^{-6}
	$\Gamma^e = \Gamma^S = \gamma$	7.467291	0.2163	13.9192	-3.0000	-3.0000	0.000138	$\lambda^e = 0.582305 \times 10^{-4}$ $\lambda^S = 0.534754 \times 10^{-6}$
Φ_{18}	None	7.467496	0.2287	13.7501	-2.9729	-3.0542	---	0.0
	$\Gamma^e = \gamma$	7.467360	0.2312	13.9178	-3.0000	-3.0590	0.000135	$+0.572685 \times 10^{-4}$
	$\Gamma^S = \gamma$	7.467496	0.2246	13.7501	-2.9729	-3.0000	$\sim 10^{-7}$	-0.239282×10^{-5}
	$\Gamma^e = \Gamma^S = \gamma$	7.467360	0.2267	13.9178	-3.0000	-3.0000	0.000135	$\lambda^e = +0.572745 \times 10^{-4}$ $\lambda^S = -0.252666 \times 10^{-5}$
Larsson's 100 term correlated function (see entry 18 Table I)		7.478025	0.2313	13.8341				

$E_{\Phi_{18}} - E_{\Phi_{10}}$, being only 0.000106 hartrees. The effect on $Q^e(0)$ is negligible also; Φ_{10} and Φ_{18} have essentially the same electron density. $Q^s(0)$, however, improves tremendously. The high stability of the final value (that of Φ_{18}) cannot be seen in Table VI but is evident from the complete table in Appendix E. From these complete results one can see certain triplet core spin terms contribute more than others to $Q^s(0)$. Only about half of the possible Θ_2 terms are necessary* but because the important ones are difficult to pick out inclusion of all of them seems advisable. Since most computer time is spent on exponent optimization the triplet core spin terms can be added practically as a bonus.

Constraining seems to be a waste of time though. In almost every case the wave function deteriorates.

$\Gamma^e = \chi$ constraints apply corrections to $Q^e(0)$ as Yue and Chong⁵⁹ found for He but the error 'improves' from $\approx -0.6\%$ to $\approx +0.5\%$ which really is not sufficient justification for cusp constraints. The Γ^e constraint is consistently the best of the three constraints imposed. Forcing $\Gamma^s = \chi$ is of little use. When several Θ_2 -type terms are present the constraints are easy to apply and properties are not changed much. When there are only a few, or none, the constraint

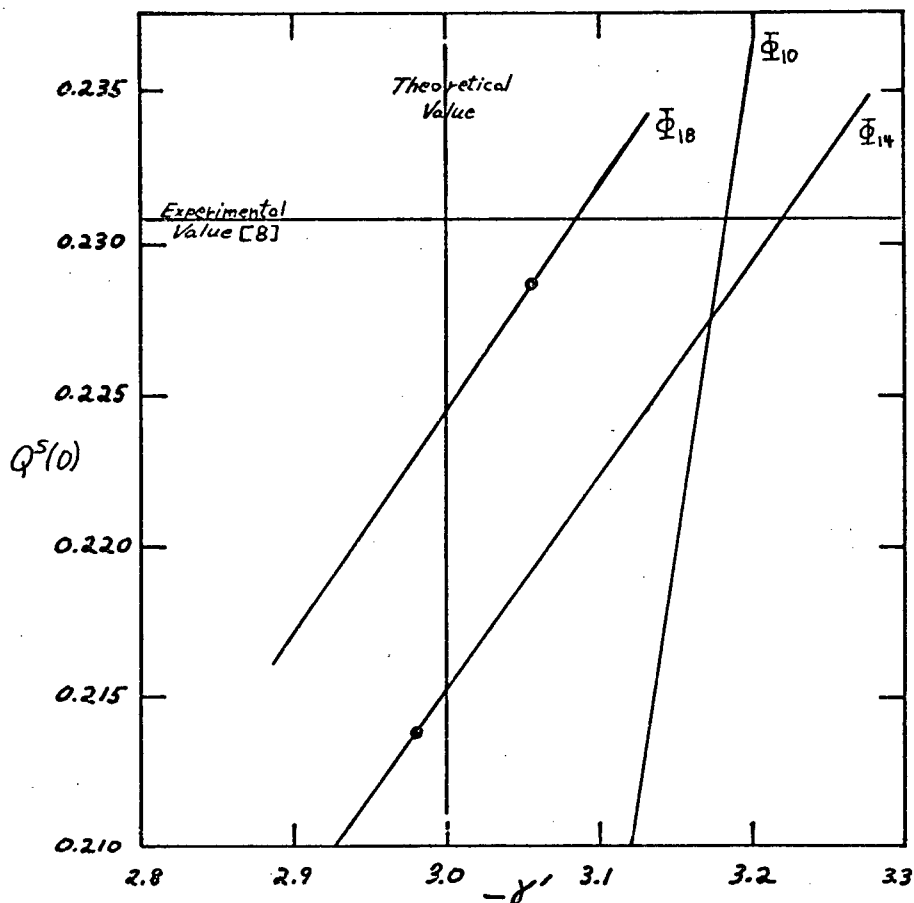
* See Φ_{14a} in Appendix E for the demonstration.

becomes more severe indicating that fine adjustments in the wave function, affecting spin properties depend on triplet core spin terms. No significance is attached to the double constraint results. Because imposing the electron cusp condition was more severe than for the spin cusp, forcing $\Gamma^e = \Gamma^s = \gamma$ invariably approximated the single constraint $\Gamma^e = \gamma$. A final point is that the free variational $Q^s(0)$ is so good for Φ_{18} that constraining would not be necessary even if it worked. No trend in improvements for $Q^s(0)$ resulting from forcing $\Gamma^s = \gamma$ can be seen from this study.

It is possible that for approximate wave functions there is an empirical 'effective' γ' rather than the theoretical $\gamma = -Z$. A further theoretical condition is $\Gamma^e = \Gamma^s$ with γ unspecified but one can confidently predict that the minimum energy for such a constraint will occur at $\Gamma^e = \Gamma^s \approx \Gamma_{\text{free variational}}^e$ for the series $\Phi_{11} \rightarrow \Phi_{18}$. To locate an effective γ' the single constraints $\Gamma^e = \gamma'$ and $\Gamma^s = \gamma'$ were imposed on several functions for different values of γ' . The actual dependence of $Q^e(0)$, $Q^s(0)$ on the cusp constraints was more evident during these calculations than in the preceding study.

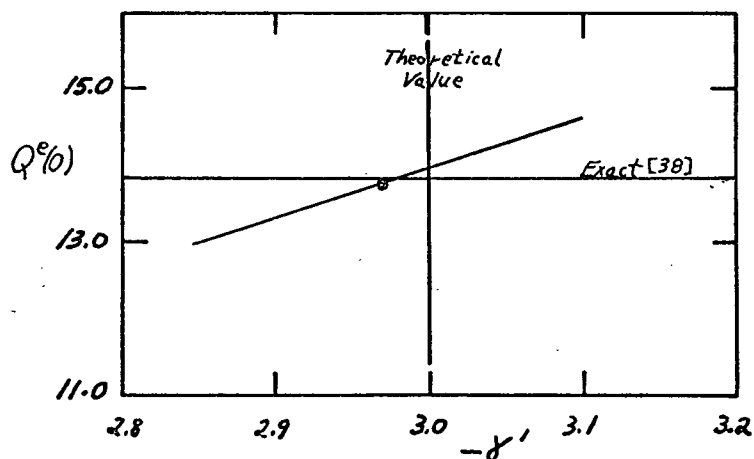
$Q^S(0)$ is shown as a function of the constraint $\Gamma^S = \gamma'$ in figure 3(A) for Φ_{10} , Φ_{14} , Φ_{18} . It has a linear dependence on Γ^S . One can see for these functions (also for all others tested) that if the free variational Γ^S is greater than $-Z = -3$ a spin cusp constraint will improve $Q^S(0)$. (Ideally the lines should pass through (0.231, -3.000)). See the complete set of properties in Appendix E to verify this. It is evident also that there is no 'effective' γ value. The scatter of points where the lines cross the experimental value (0.2313) precludes this. A similar graph of $Q^e(0)$ versus $\Gamma^e = \gamma'$ in figure 3(B) also shows a linear dependence. That the Θ_2 -type terms do not influence $Q^e(0)$ is obvious; the lines for all functions, Φ_{10} , Φ_{14} , Φ_{18} , are superimposed. Why $\Gamma^e = -Z$ overcorrects $Q^e(0)$ is clear for these cases. An effective γ' for $Q^e(0)$ cannot be said to exist even though all lines pass $Q^e(0) = 13.83$ [38] at $\gamma' = -2.985$ because the functions Φ_{10} through Φ_{18} are all too similar in electron density. A comparison of figures 3(A) and 3(B) will affirm that calculation is more difficult for $Q^S(0)$ than $Q^e(0)$ and will reflect the scatter of $Q^S(0)$ values in Table I. Figure 4, (A)

Figure 3. (A) $Q^s(0)$ as a function of the constraint^a
 $\Gamma^s = \gamma'$ for Φ_{10} , Φ_{14} , Φ_{18} .



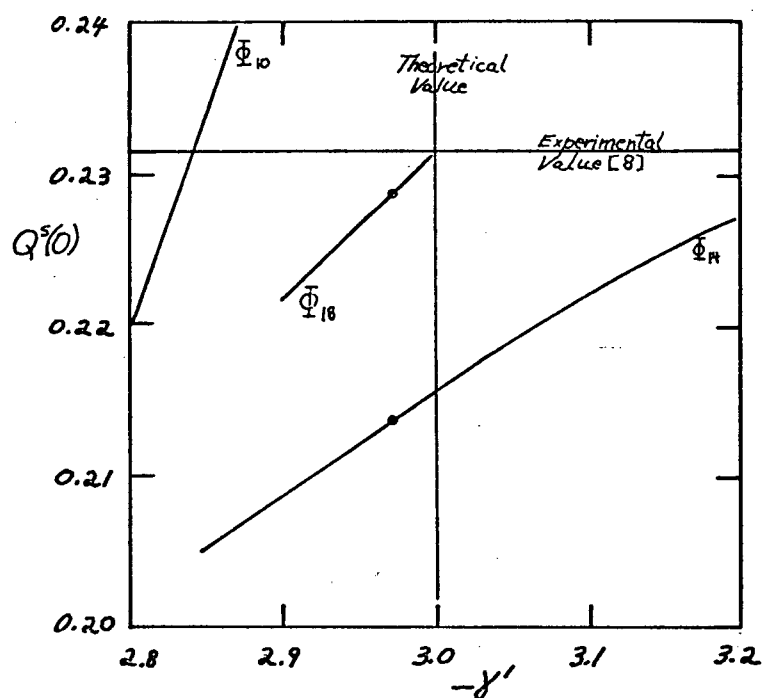
^aFree variational values are marked explicitly for
 Φ_{14} , Φ_{18} .

(B) $Q^e(0)$ as a function of the constraint^b
 $\Gamma^e = \gamma'$ for Φ_{10} , Φ_{14} , Φ_{18} .



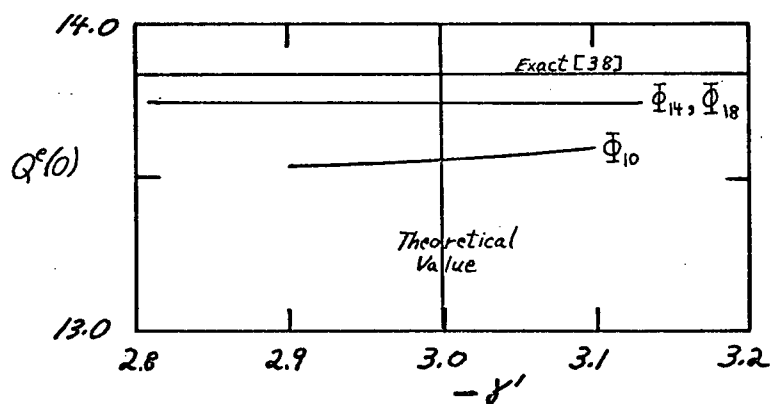
^bThe common free variational value is marked explicitly.

Figure 4. (A) $Q^s(0)$ as a function of the constraint^a
 $\Gamma^e = \gamma'$ for Φ_{10} , Φ_{14} , Φ_{18} .



^aFree variational values are marked for Φ_{14} , Φ_{18} .

(B) $Q^e(0)$ as a function of the constraint
 $\Gamma^s = \gamma'$ for Φ_{10} , Φ_{14} , Φ_{18} .



and (B), shows $Q^S(0)$ as a function of $\Gamma^e = \gamma'$ and $Q^e(0)$ as a function of $\Gamma^s = \gamma'$. Previous conclusions are borne out: 1) The spin cusp constraint adjusts only minute details of a wave function without affecting $Q^e(0)$ at all. 2) The electron cusp constraint is not likely to improve spin densities. Finally it must be concluded that these diagonal cusp constraints are not useful for improving $Q^S(0)$. If non-linear parameters are optimized and Θ_2 -type spin terms are included the wave function should have a good spin density at the nucleus without any constraint.

3.4 Off-diagonal cusp constraints with weighting functions

Since attempts thus far to apply the philosophy of constrained variation towards calculating better spin densities have failed, the problem must be re-examined. If $\Phi_{s,M}$ satisfies nuclear cusp conditions the integration in (2.4.5) can be seen as an artifact, merely allowing an evaluation of the expression

$$\lim_{r_i \rightarrow 0} \left(\frac{\partial}{\partial r_i} - \gamma \right) \Phi_{s,M} \quad (3.4.1)$$

(Compare with (2.3.1)). Replacement of $\Phi_{s,M}^*$ in (2.4.5) by an arbitrary function, f^* , seems reasonable in this light. To apply this new concept,

restrictions on f must be examined.

If ψ is a spatial eigenfunction satisfying (2.3.8) for the case of nuclear cusp, the condition

$$\int f^* (\mathcal{L}_{\lambda=0}^a - \gamma \mathcal{L}_{\lambda=0}^a) \psi d\tau = 0, \quad a=e,s \quad (3.4.2)$$

is valid for any well-behaved function f . Spin must be included in f when the spin containing function $\Phi_{S,M}$ is considered because integration over a single spin variable is undefined. To avoid trivial conditions f should be an eigenfunction of \mathcal{S}^2 and \mathcal{S}_z with the same spin functions Θ_i as $\Phi_{S,M}$. Then

$$\langle f | \{ \mathcal{L}_{\lambda=0}^a - \gamma \mathcal{L}_{\lambda=0}^a \} | \Phi_{S,M} \rangle = 0 \quad (3.4.3)$$

is valid. (Compare with (2.4.5)). This suggests the off-diagonal nuclear cusp constraints,

$$\langle f | \mathcal{C} | \psi \rangle = \langle f | \{ \mathcal{L}_{\lambda=0}^a - \gamma \mathcal{L}_{\lambda=0}^a \} | \psi \rangle = 0, \quad a=e,s \quad (3.4.4)$$

on an approximate ψ . The function, f , can be thought of as a weighting function. In particular f may be antisymmetric with respect to interchange of electron coordinates. If $f = \psi$ the diagonal

cusped constraint (3.2.1) is recovered.

The traditional approach to constrained variation, described in the text at equation (3.1.1), forces

$\langle C_i \rangle = 0$. In the working basis set, $\{\xi_k\}$, (usually the basis of free variational eigenvectors) this relation is expressed in matrix notation

$$a^+ C_i a = 0. \quad (3.4.5)$$

a is the constrained (column) eigenvector sought,

$$\psi = \sum_i a_i \xi_i,$$

and $C_i = [C_{kl,i}]$, $C_{kl,i} = \langle \xi_k | C_i | \xi_l \rangle$. (3.4.6)

In contrast, the method of Weber and Handy⁶⁹ minimizes energy while constraining

$$p_i^+ a = 0 \quad (3.4.7)$$

where p_i is a column vector containing necessary information about the i^{th} constraint condition.

In the off-diagonal case, (3.1.6) can be expanded in a basis $\{\xi'_k\}$ as

$$\mathcal{L}^+ \mathcal{C}_i a = 0 \quad (3.4.8)$$

for $\phi = \sum_k \mathcal{L}_k \mathcal{E}'_k$. Then

$$p_i = \mathcal{L}^+ \mathcal{C}_i, \quad \mathcal{C}_i = [C_{kl,i}], \quad C_{kl,i} = \langle \mathcal{E}'_k | \mathcal{L}^q - \delta \mathcal{L}^q | \mathcal{E}_l \rangle \quad (3.4.9)$$

Note the important distinction between (3.4.9) with (3.4.6), and (3.1.2). The procedure of Weber and

Handy does not need an Hermitian \mathcal{C} operator. If

\mathcal{L} is fixed, the constraints, $p_i a$, are imposed in a one-step matrix diagonalization procedure. The diagonal constraint case, (3.4.5), can be handled, but an iteration procedure on a is necessary:

$$a_{k-1}^+ \mathcal{C}_i a_k = 0, \quad (3.4.10)$$

$$a_0 = \mathcal{L}.$$

Several types of weighting functions were tested to determine their effect on $Q^S(0)$ and $Q^e(0)$. The first tried was $f = \mathcal{E}_k$, $\{\mathcal{E}_k\}$ the set of free variational eigenvectors. Since the $\{\mathcal{E}_k\}$ are energy ordered

$$\langle \mathcal{E}_k | H | \mathcal{E}_k \rangle = E_k \langle \mathcal{E}_k | \mathcal{E}_k \rangle, \quad E_k \leq E_{k+1}$$

the constraint (3.4.4) amounts to weighting by energy.

Computations are simple for this choice because the matrix elements (3.4.9), $\langle \xi_k' | \{Y - r_2\} | \xi_l \rangle = \langle \xi_k | \{Y - r_2\} | \xi_l \rangle$ had been evaluated for diagonal constraints. The results of weighting $\bar{\Phi}_{14}$ with selected* ξ_k

$$\langle \xi_k | G^a | \psi \rangle = 0, \quad a = e, s$$

are presented in Table VII. Both electron and spin cusp single constraints and the double constraint were carried out (for $\gamma = -Z$). The values of $\Gamma^{e,s}$ are included so the consequences of $f = \xi_i$, the groundstate eigenvector, can be seen. In all three cases, (e), (s), (e,s), $f = \xi_i$ closely duplicated the results of the diagonal constraints in section.3.3, Table VI. The appropriate $\Gamma^{e,s}$ equal -Z to within 3-4 decimal places.** Constrained energies are the same to 10^{-6} hartree and $Q^e(0)$, $Q^s(0)$ values also only differ in the 3rd, 4th decimal places. This is to be expected since the overwhelming contribution to the constrained $\bar{\Phi}_{14}$ is ξ_i . (See equation (3.1.8)). The significance is that the off-diagonal, one-step method of Weber and Handy can be used to

* Realize that the groundstate of $\bar{\Phi}_{14}$ is ξ_i . $\bar{\Phi}_{14}$ changes to some $\psi \neq \xi_i$ when constrained.

** This shows that the integral cusp conditions are only necessary, for if the correct cusp existed, $\Gamma \equiv \gamma$ always.

Table VII. Energy weighted off-diagonal cusp constraints on Φ_{14} .

Constraint	Weighting Function	-E	$\Delta E \times 10^6$	$Q^s(0)$	$Q^e(0)$	Γ^e	Γ^s
None	---	7.467429	---	0.2136	13.7500	-2.9728	-2.9790
a=e	ξ_1	7.467291	138	0.2152	13.9211	-3.0000	-2.9860
"	ξ_2	7.467429	0	0.2137	13.7502	-2.9728	-2.9808
"	ξ_3	7.467390	39	0.1668	13.7575	-2.9742	-2.1698
"	ξ_7	7.467251	178	0.2100	13.5580	-2.9426	-2.9445
"	ξ_{14}	7.466214	1215	0.1839	14.2010	-3.0468	-2.4299
a=s	ξ_1	7.467429	0	0.2150	13.7500	-2.9728	-2.9999
"	ξ_2	7.467199	230	0.0810	13.7287	-2.9698	+1.9146
"	ξ_3	7.467248	181	0.1387	13.6719	-2.9611	-1.4761
"	ξ_7	7.467429	0	0.2154	13.7500	-2.9728	-3.0053
"	ξ_{14}	7.467427	2	0.2001	13.7509	-2.9729	-2.7689
a=e,s	ξ_1	7.467291	138	0.2162	13.9211	-3.0000	-2.9999
"	ξ_2	7.467167	262	0.0660	13.7301	-2.9704	+3.6892
"	ξ_3	7.467162	267	0.1860	13.5676	-2.9445	-2.6295
"	ξ_7	7.467250	179	0.2153	13.5579	-2.9426	-3.0185
"	ξ_{14}	7.466202	1227	0.2144	14.2055	-3.0475	-2.9572

closely duplicate the results of any diagonal constraint providing (3.1.8) holds. Computational problems described in 3.2 are bypassed and no iteration is necessary. The weighting method with $f = \xi_i$ thus seems ideal for pre-testing the effects of various constraints. As far as weighting with other energy eigenfunctions is concerned, $f = \xi_K$, $K > 1$, unpredictable, random, poor results occur.

Configuration weighting was next attempted. Configurations, $\{\psi_i\}$, have an energy associated with them but they are more spatial in character than the energy eigenfunctions $\{\xi_K\}$, ($\xi_K = \sum_l a_{Kl} \psi_l$). Putting $f = \psi_i$ is a kind of spatial weighting. Again, results are random and meaningless and will not even be presented.

Application of Weber and Handy's method to the diagonal cusp constraint case with (3.4.10) was investigated. If convergence* was rapid, computational problems of the sort mentioned in 3.2 would be avoided and the exact diagonal constraint $\langle \psi | \mathcal{C} | \psi \rangle = 0$ would be imposed. After convergence was achieved slight differences from the pure diagonal approach (3.1.1) were found even though $\Gamma = \delta$ from both methods.

* The initial guess $Q_0 = \xi_i$, in (3.4.10) did not converge when an Hermitian \mathcal{C} was used but oscillated back to $Q_{2K} = \xi_i$. Groundstate energy and the overlap $\langle a^\dagger a \rangle$ were employed as convergence criteria.

A comparison of the two approaches to diagonal constraints for Φ_{14} is presented in Table VIII for academic interest. The reason for the anomalous results was not a program error but imposition of a different constraint. For the pure, original diagonal technique the constraint matrix $C = P + P^+$ was unambiguously employed. The Hermitian constraint matrix that developed during iteration had the form

$$P^+ Q Q^+ + Q Q^+ P$$

where Q is the constrained eigenvector and need not equal a , the constrained eigenvector for the first case. Both these eigenvectors give the condition

$$a^+ P a = Q^+ P Q = 0 \quad \text{or} \quad \Gamma = \delta.$$

A final exploration of the weighting concept employed $f = W(\rho)$, where $W = A (\chi_{1s}(1)\alpha(1)\chi_{1s}(2)\beta(2)\chi_{2s}(3)\alpha(3))$, the χ_{ns} 's are STO's having orbital exponents

$S_{1s} = 2.7 \rho$, $S_{2s} = 1.3 \rho$. ρ is a variable parameter. The values of S_{1s} , S_{2s} for $\rho = 1$ were chosen with Slater's rules. Now the wave function to be constrained can be weighted in selected regions. Of special interest is the extrapolation $\rho \rightarrow 0$.

Table VIII. Comparison of the diagonal and off-diagonal iterative methods for diagonal constraints.

Example: Φ_{14} , $\Gamma^e = \gamma$ constraint

Wave function attribute	diagonal method (see equation (3.4.5))	iterative method (see equation (3.4.10))
Energy	- 7.4672914	- 7.4672913
$Q^S(0)$	0.215387	0.215193
$Q^e(0)$	13.919166	13.920945
Γ^e	- 3.000000	- 3.000000
Γ^s	- 2.986952	- 2.985937
a_1^*	+ 0.9999931	+ 0.9999933
a_2	- 0.1996x10 ⁻³	- 0.1757x10 ⁻³
a_3	+ 0.2666x10 ⁻³	+ 0.2446x10 ⁻³
a_4	+ 0.2031x10 ⁻⁴	+ 0.2099x10 ⁻⁴

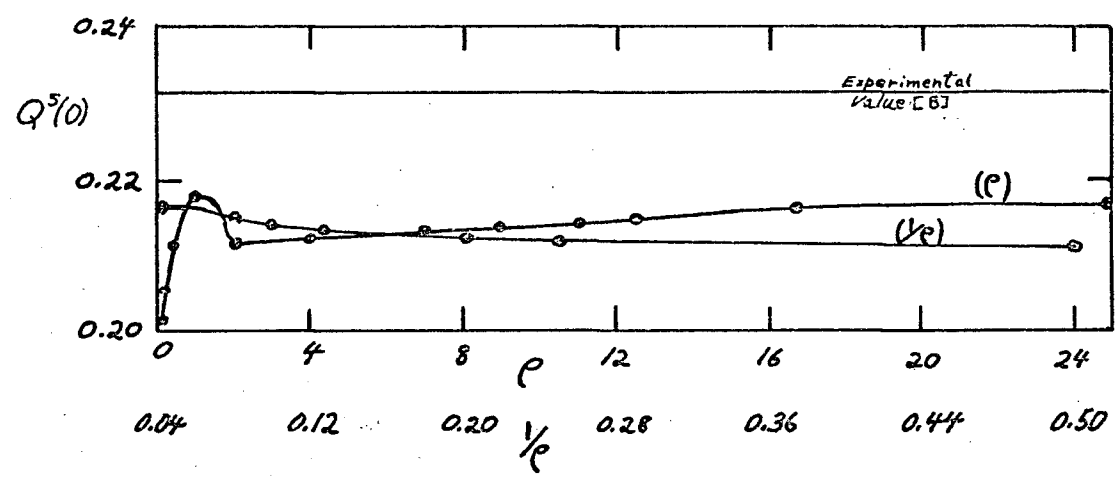
* a_i = coefficient in constrained wave function of the i^{th} free variational eigenfunction.

W becomes a Dirac δ -like function, weighting the nuclear regions to an extreme degree. $Q^s(0)$ is plotted against ρ and $1/\rho$ in figure 5(A). Figure 5(B) shows the corresponding relations of $Q^e(0)$ for electronic cusp constraints on Φ_{14} . Negative results are obtained. A sampling of the corresponding results for spin cusp constraints is shown in Table IX. An interesting maximum exists around $\rho = 1/4$ but is certainly coincidental. Similar studies were carried out on Φ_{10} and Φ_{17} of the same series of functions with the same discouraging results. Energy sacrifices, except for the obviously distorted cases, were negligible.

Investigation of multiple weighting constraints is important because if (3.4.4) is true for all members of a complete set, an approximate wave function must have the correct cusp. Thus if $\langle f_i | \{ \mathcal{G}^2 - \delta^2 \} | \psi \rangle$ is forced to be zero for many f_i functions perhaps

ψ will more closely satisfy the nuclear cusp condition. The method of Weber and Handy simplifies constraint calculations. Different weights were applied simultaneously to Φ_{10} , Φ_{14} and Φ_{17} . Combinations of $W(\rho)$, and ξ_i , the free variational eigenfunction, were used in both electronic and spin cusp constraints. Representative results for Φ_{14} are presented in Table X. Use of the diagonal iteration technique to force

Figure 5. (A) $Q^S(0)$ plotted against ρ and $1/\rho$ in weighting electronic cusp constraint on $\bar{\Phi}_{14}$.



(B) $Q^e(0)$ plotted against ρ and $1/\rho$ in weighting electronic cusp constraint on $\bar{\Phi}_{14}$.

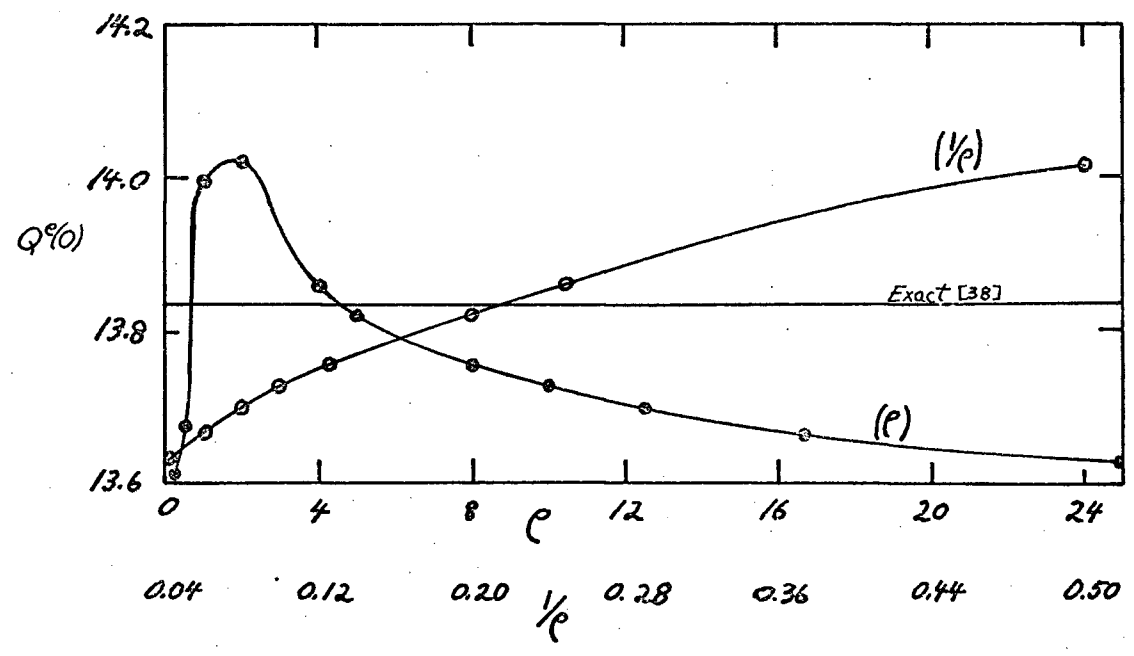


Table IX. $Q^S(0)$, $Q^e(0)$ for the off-diagonal weights
 $W(\rho)$ in spin cusp constraints of Φ_{14} .

ρ	$Q^S(0)$	$Q^e(0)$
25	-0.1307	13.6474
10	-0.2005	13.7062
8	-0.1243	13.7244
5	+0.0381	13.7443
2	+0.1817	13.7499
1	+0.2144	13.7500
1/2	+0.2260	13.7503
1/4	+0.2233	13.7505
1/8	+0.2148	13.7501
Free variational results	0.2135	13.7500

Table X. Multiple weighting constraints on Φ_{14} .

Number of simultaneous constraints	Constraints*	ΔE (energy sacrifice due to constraints)	$Q^s(0)$	$Q^e(0)$
3	$W^s(\frac{1}{2}), W^s(2), W^s(4)$	0.0135	0.0983	13.6157
3	$\xi_1^s, W^s(\frac{1}{2}), W^s(2)$	0.0140	0.0662	13.2261
2	$\xi_1^s, W^s(\frac{1}{2})$	0.0000	0.2181	13.7517
2	$\xi_1^s, W^s(2)$	0.0001	0.2227	13.7513
2	$W^s(\frac{1}{2}), W^s(2)$	0.0001	0.2094	13.7519
3	$W^e(\frac{1}{2}), W^e(2), W^e(4)$	0.0018	0.1968	13.9758
3	$\xi_1^e, W^e(\frac{1}{2}), W^e(2)$	0.0009	0.2052	13.8953
2	$\xi_1^e, W^e(\frac{1}{2})$	0.0009	0.2038	13.8998
2	$\xi_1^e, W^e(2)$	0.0009	0.2083	13.8952
2	ξ_1^e, ξ_1^s	0.0001	0.2162	13.9211
4	$\xi_1^e, \xi_1^s, W^e(\frac{1}{2}), W^s(\frac{1}{2})$	0.0009	0.2205	13.8990
6	$\xi_1^e, \xi_1^s, W^e(\frac{1}{2}), W^s(\frac{1}{2}), W^e(2), W^s(2)$	0.0177	0.0407	13.7131

* $W^a(p)$ or ξ_1^a , $a = e, s$ gives the type of constraint applied.

$\langle \psi | G | \psi \rangle = 0$ along with $\langle W(P) | G | \psi \rangle = \dots = 0$ did not produce significantly different results from the case $\langle S_1 | G | \psi \rangle = \langle W(P) | G | \psi \rangle = \dots = 0$ as expected. No definite trends could be determined. The extreme number of possible constraints also confuses the problem.

In conclusion, off-diagonal weighting constraints have offered no sure method for improving spin and electron densities. A more realistic form for $W(P)$ is $A(\chi_{1s}(P_1) \alpha \chi_{1s}(P_2) \beta \chi_{2s}(P_3) \alpha)$, weighting only one electron at a time but this was not tried. The general technique could perhaps be improved conceptually and might be useful for other properties.

CHAPTER IV

SUFFICIENT CONDITIONS FOR CORRECT CUSP

4.1 Theory

The failure of necessary cusp constraints to provide accurate descriptions of wave functions at nuclear coalescence is by now obvious. That these constraints need not force the correct behaviour at the cusp is re-emphasized. The weighting constraint results in Chapter III demonstrate this fact. Constraining Ψ , $\langle f/g - \gamma^2/\Psi \rangle = 0$ does not guarantee $\langle \Psi/g - \gamma^2/\Psi \rangle = 0$ as would be found if Ψ had the proper cusp. Are there practical, sufficient restrictions on a function that will provide the correct cusp? For an answer a return to first principles is indicated.

The necessary and sufficient nuclear coalescence conditions in differential form for any wave function are embodied in (2.3.8a),

$$\left(\frac{\partial \frac{1}{F_k} \hat{\Phi}}{\partial F_k} \right)_{F_k=0} = \frac{\gamma}{1+\lambda} \left(\frac{1}{F_k} \hat{\Phi} \right)_{F_k=0} \quad (4.1.1) \approx (2.3.8a)$$

and hold in turn for each electron ($K = 1, N$). Define an operator

$$p_\lambda(k) = \lim_{r_k \rightarrow 0} \left(\frac{\partial}{\partial r_k} - \frac{\lambda}{1+\lambda} \right) \frac{1}{r_k^\lambda} I(k) \quad (4.1.2)$$

where

$$I(k) = \frac{1}{4\pi} \sum_{m=-\lambda}^{+\lambda} \int_{r_k=\text{constant}} d\Omega_k Y_{\lambda m}^*(\theta_k, \phi_k) \quad (4.1.3)$$

takes the spherical average about the point of coalescence of the K^{th} electronic coordinates as in (2.3.8a).

$p_\lambda(k)$ is a one-electron cusp evaluation operator.

The nuclear coalescence conditions of a spinless wave function satisfying (2.3.8) are written concisely,

$$p_\lambda(k) \Phi = 0 \quad (4.1.4)$$

Extension to spin-space is straightforward. The nuclear coalescence condition for an exact spin-containing function (see (2.3.11)) is

$$p_\lambda(k) \Phi_{S,M} = \sum_i (p_\lambda(k) \psi_k) \theta_k = 0 \quad (4.1.5)$$

as each ψ_k satisfies (4.1.4). An approximate wave function with spin, Ψ , has the correct cusp if and

only if

$$p_{\lambda}(k) \underline{\Psi} = 0 . \quad (4.1.6)$$

The present discussion will be limited to nuclear cusp conditions for CI wave functions. That is, λ equals zero (and will be suppressed). Specialized conditions derived from (4.1.6) will be only sufficient because a configuration interaction expansion is not a unique functional form.

An n-term CI function with sharp spin and orbital angular momentum and sharp Z components--an eigenfunction of \mathcal{S}^2 , \mathcal{L}^2 , \mathcal{S}_z , \mathcal{L}_z --is usually expanded in the form

$$\underline{\Psi}_{CI} = \sum_{i=1}^n c_i \underline{\Psi}_i \quad (4.1.7)$$

The $\{c_i\}$ are variationally determined linear coefficients. The $\{\underline{\Psi}_i\}$ are eigenfunctions of \mathcal{S}^2 , \mathcal{L}^2 , \mathcal{S}_z , \mathcal{L}_z having the same eigenvalues as $\underline{\Psi}_{CI}$ and are described by a predetermined, fixed linear combination of Slater determinants $\{\phi_k\}$,

$$\underline{\Psi}_i = \sum_l a_{il} \phi_l . \quad (4.1.8)$$

Since $p(k)$ operates only on the K^{th} electron each Slater determinant is conveniently expanded into cofactors of the one-electron functions for the K^{th} electron:

$$\begin{aligned} \phi_{\ell} &= \begin{vmatrix} \chi_1^{\ell}(1) S_1^{\ell}(1) & \chi_2^{\ell}(1) S_2^{\ell}(1) & \chi_3^{\ell}(1) S_3^{\ell}(1) \\ \chi_1^{\ell}(2) S_1^{\ell}(2) & \chi_2^{\ell}(2) S_2^{\ell}(2) & \chi_3^{\ell}(2) S_3^{\ell}(2) \\ \chi_1^{\ell}(3) S_1^{\ell}(3) & \chi_2^{\ell}(3) S_2^{\ell}(3) & \chi_3^{\ell}(3) S_3^{\ell}(3) \end{vmatrix} \\ &= \sum_{m=1}^3 \chi_m^{\ell}(k) S_m^{\ell}(k) \phi_{\ell m}^K \end{aligned} \quad (4.1.9)$$

where $S_m^{\ell}(k) = \alpha$ or β and $\phi_{\ell m}^K$ is the cofactor in ϕ_{ℓ} of the K^{th} row and m^{th} column. $\phi_{\ell m}^K$ is thus a function of all electronic and spin coordinates but those of the K^{th} electron. The explicit case for lithium has been depicted to avoid notational difficulties.

The superscript ℓ is added when needed to distinguish the one-electron orbitals belonging to different determinants. In this work only STO's, $\{\chi_i\}$ (defined in (3.1.7)), are considered although the approach can be developed for any basis set. The Pauli principle makes the choice of K irrelevant. Operating on (approximate) Ψ_{CI} with the cusp evaluation operator one obtains

$$p(k) \Psi_{CI} = \sum_{i, \ell, m} c_i a_{i\ell} p(k) \chi_m^{\ell}(k) S_m^{\ell}(k) \phi_{\ell m}^K \quad (4.1.10)$$

which must equal zero if the cusp is correct.

In general, $S_m^{\ell}(k) \phi_{\ell m}^K \neq 0$, unless there is a linear dependence in the set $\{\chi_i\}$. Sufficient conditions for cusp satisfaction are found by letting the coefficient of $S_m^{\ell}(k) \phi_{\ell m}^K$ equal zero for each ℓ, m ,

$$p(k) \chi_m^{\ell}(k) \sum_i c_i a_{i\ell} = 0. \quad (4.1.11)$$

The system of equations, $\sum_i c_i a_{i\ell} = 0$, $\ell = 1, \dots$, # of determinants, leads trivially to an identically zero wave function. This means that $p(k) \Psi_{cr} = 0$ when $p(k) \chi_m^{\ell}(k) = 0$ for each member of the set, $\{\chi_i\}$.

The expression

$$p(k) \chi_m^{\ell}(k) = 0 \quad (4.1.12)$$

is an orbital cusp condition and must be evaluated explicitly to find the conditions for STO's:

$$p_{\lambda=0} \chi_{n\ell m}(r, \theta, \phi) = \lim_{r \rightarrow 0} \left(\frac{\partial}{\partial r} - \gamma \right) \times \frac{1}{4\pi} \int d\Omega_i \left\{ N_n \times r^{n-1} e^{-\gamma r} Y_{\ell m}(\theta, \phi) \right\} \quad (4.1.13)$$

The discussion can be restricted to s-type orbitals since the spherical averaging operator ensures that all STO's with $\ell > 0$ automatically satisfy (4.1.12).

Equation (4.1.13) reduces to

$$\rho \chi_{ns} = \begin{cases} -\chi_{1s}(0)(\rho + \delta) & n=1 \\ + \left(\frac{\chi_{2s}}{r} \right)_{r=0} & n=2 \\ 0 & n \geq 3 \end{cases} \quad (4.1.14)$$

For the orbital cusp condition to hold,

- (1) $\rho \chi_{1s} \equiv 0$ implying $\rho = -\delta = Z$,
- (2) $\rho \chi_{2s} \equiv 0$ is not possible, (4.1.14a)
- (3) $\rho \chi_{n\ell m} \equiv 0$ is satisfied for all orbitals except χ_{1s} , χ_{2s} .

These are precisely the conditions (2.5.1), (2.5.2) given for STO's by Roothaan and Kelly⁶⁵ with a different derivation when only cusp conditions ($\lambda = 0$) are considered. The present treatment can easily be extended to include coalescence conditions.

Another approach exists. Examine (4.1.10). If any cofactors are equal, $\phi_{\ell m}^K = \phi_{\ell' m'}^K = \dots$, there will be other relationships to investigate. A more general expression of (4.1.10) is

$$\rho(k) \psi_{cr} = \sum_{\ell, m} \left[\sum_{i, \ell', m'} (c_i a_{i\ell'} \rho(k) \chi_{m'}^{\ell'}(k) \times S_{\ell}^m(k) \phi_{\ell m}^K) \right], \quad (4.1.15)$$

$$S_{m'}^{\ell'}(k) \phi_{\ell' m'}^K = S_{\ell}^m(k) \phi_{\ell m}^K \quad \text{for all } \ell', m'.$$

All equal cofactors, and spins for the K^{th} electron, have been factored out. Two explicit cases are now presented to show what is involved; (4.1.15) is too indeterminate to give recognizable cusp conditions:

Case 1

The simplest possible case has a basis of three STO's--a, a', b ($a \neq a'$). The Slater determinants are defined

$$\begin{aligned}\phi_1 &= (a(1)\alpha(1), b(2)\beta(2), b(3)\alpha(3)) \equiv (a, \bar{b}, b) \\ \phi_2 &= (a'(1)\alpha(1), b(2)\beta(2), b(3)\alpha(3)) \equiv (a', \bar{b}, b) \quad (4.1.16)\end{aligned}$$

The notation is short for (4.1.9), identifying a determinant by its principle diagonal. χ and $\bar{\chi}$ within the brackets in (4.1.16) imply the spin-orbitals $\chi\alpha$ and $\chi\beta$ respectively. The CI function appears

$$\Psi_{CI} = c_1 \psi_1 + c_2 \psi_2 ; \quad \psi_1 = \phi_1, \quad \psi_2 = \phi_2 . \quad (4.1.17)$$

(The sum (4.1.8) has but one term). Now $\phi_{11}^K = \phi_{21}^K$ and (4.1.15) reduces to

$$\begin{aligned}
\rho(k) \Psi_{cT} &= \rho(k) \left\{ c_1 (a\alpha\phi_{11}^k + b\beta\phi_{12}^k + b\alpha\phi_{13}^k) \right. \\
&\quad \left. + c_2 (a'\alpha\phi_{21}^k + b\beta\phi_{22}^k + b\alpha\phi_{23}^k) \right\} \\
&= [\rho(k)(c_1 a(k) + c_2 a'(k))] \alpha(k) \phi_{11}^k \\
&\quad + [\rho(k)b(k)] \left\{ \beta(k)(c_1 \phi_{12}^k + c_2 \phi_{22}^k) \right. \\
&\quad \left. + \alpha(k)(c_1 \phi_{13}^k + c_2 \phi_{23}^k) \right\}
\end{aligned}
\tag{4.1.18}$$

To find the cusp conditions for this function equate to zero coefficients of $\phi_{\ell m}^k$ for all ℓ, m .

$$(1) \quad p b = 0$$

$$(2) \quad p [c_1 a + c_2 a'] = 0 \tag{4.1.19}$$

Equation (1) implies that if $p \Psi = 0$, orbital b must satisfy the orbital cusp condition, (4.1.12). That is, b must fit into the scheme (4.1.14a). Such STO's will be written $\underline{\chi}_i$. Thus $p \underline{b} \equiv 0$ and \underline{b} is chosen by the rules (4.1.14a). Equation (2) fixes the ratio* between c_1 and c_2 :

* Note that $p \chi$ is a constant; all functional dependences have been removed.

$$\frac{c_2}{c_1} = -\frac{pa}{pa'} \quad (4.1.20)$$

a, a' must not satisfy the orbital cusp condition if new relations are to be found. (If $pa \equiv 0$, but $pa' \neq 0$ the function, ψ_{CI} , collapses to a single term). Of course there are no longer secular equations for this case:

$$\psi_{CI} = c_1 \left(\psi_1 - \frac{pa}{pa'} \psi_2 \right) \quad (4.1.21)$$

If $b = \chi_{nem}$, $l > 0$, the set of orbitals having sharp L_z , ($m = \pm l, \pm l-1, \dots, 0$), may need to be included in the basis ensuring sharp total angular momentum for ψ_{CI} . If ψ_{CI} has 2S symmetry this particular example covers only the cases

$$\mathcal{L} = \begin{cases} \chi_{1s} & S_b = Z \\ \chi_{ns} & n > 2 \end{cases}$$

Case 2

No basis orbital needs to satisfy the orbital cusp condition in this example. The Slater determinants, $\{\phi_i\}$, and eigenfunctions of S^2 , L^2 , S_z , L_z for a 2S function, $\{\psi_i\}$, are listed in Table XI. Only $\Theta, -$ type terms are included in $\{\psi_i\}$;

Table XI. The set of Slater determinants, $\{\phi_i\}$,
and eigenfunctions, $\{\psi_i\}$ of S^2 , L^2 ,
 S_z , L_z for the 2S wave function described in case 2 of section 4.1.

$\phi_1 = (a, \bar{b}, c)$	$\phi_9 = (a', \bar{b}', c)$
$\phi_2 = (b, \bar{a}, c)$	$\phi_{10} = (b', \bar{a}', c)$
$\phi_3 = (a', \bar{b}, c')$	$\phi_{11} = (a', \bar{b}, c')$
$\phi_4 = (b, \bar{a}', c')$	$\phi_{12} = (b, \bar{a}', c')$
$\phi_5 = (a, \bar{b}', c)$	$\phi_{13} = (a, \bar{b}', c')$
$\phi_6 = (b', \bar{a}, c)$	$\phi_{14} = (b', \bar{a}, c')$
$\phi_7 = (a, \bar{b}, c')$	$\phi_{15} = (a', \bar{b}', c')$
$\phi_8 = (b, \bar{a}, c')$	$\phi_{16} = (b', \bar{a}', c')$
$\psi_1 = \phi_1 + \phi_2$	$\psi_5 = \phi_9 + \phi_{10}$
$\psi_2 = \phi_3 + \phi_4$	$\psi_6 = \phi_{11} + \phi_{12}$
$\psi_3 = \phi_5 + \phi_6$	$\psi_7 = \phi_{13} + \phi_{14}$
$\psi_4 = \phi_7 + \phi_8$	$\psi_8 = \phi_{15} + \phi_{16}$

addition of triplet core spin terms will be demonstrated shortly. Any different set $\{\phi_i\}$ will cause a breakdown in the following equations. The CI function is

$$\Psi_{CI} = \sum_{i=1}^8 c_i \Psi_i .$$

If $\nabla(k) \Psi_{CI} = 0$, either each element of $\{\chi_i\}$ must obey the orbital cusp condition, $\{\chi_i\} \equiv \{\underline{\chi}_i\}$, or the following set of equations must be satisfied:

$$\begin{pmatrix} \alpha & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ \gamma & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & \beta & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & \gamma & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & \alpha & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & \gamma & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \alpha & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & \beta & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & \gamma & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & \beta & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & \alpha & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \\ c_7 \\ c_8 \end{pmatrix} = 0 \quad (4.1.22)$$

where $\alpha = \frac{pa}{pa}$, $\beta = \frac{pb}{pb}$, $\gamma = \frac{pc}{pc}$. There

are seven linearly independent equations and eight unknowns. The solutions to a constant (normalization) factor are:

$$\begin{array}{ll}
c_1 = 1 & c_5 = \alpha\beta \\
c_2 = -\alpha & c_6 = \alpha\gamma \\
c_3 = -\beta & c_7 = \beta\gamma \\
c_4 = -\gamma & c_8 = -\alpha\beta\gamma
\end{array} \quad (4.1.23)$$

The linear coefficients have been completely fixed.

From previous experience triplet core spin terms should be included. Table XII contains the additional elements needed in Table XI for $\{\phi_i\}$ and $\{\psi_i\}$. If all possible Θ_2 -type terms are not included the equations will breakdown. Now

$$\psi_{CI} = \sum_{i=1}^{16} c_i \psi_i .$$

The only variationally determined linear parameter, k , couples the Θ_1 and Θ_2 terms. The coefficient sets $\{c_1 \rightarrow c_8\}$, and $\{c_9 \rightarrow c_{16}\}$ are both defined by the equations (4.1.22), the solutions being

$$\begin{cases} c_i, & i = 1, 8 \text{ as in (4.1.23)} \\ c_{i+8} = kc_i, & i = 1, 8 \end{cases} \quad (4.1.24)$$

Other cases, with various combinations of the sets $\{\chi_i\}$ and $\{\underline{\chi}_i\}$, lead to similar results. Always

Table XII. Additional $\{\phi_i\}$ and $\{\psi_i\}$ elements for
Table XI when Θ_2 -type spin terms are
included.

$\phi_{17} = (a, \bar{c}, b)$	$\phi_{21} = (a', \bar{c}, b')$
$\phi_{18} = (a', \bar{c}, b)$	$\phi_{22} = (a', \bar{c}', b)$
$\phi_{19} = (a, \bar{c}, b')$	$\phi_{23} = (a, \bar{c}', b')$
$\phi_{20} = (a, \bar{c}', b)$	$\phi_{24} = (a', \bar{c}', b')$

$\psi_9 = \phi_1 - \phi_2 + 2\phi_{17}$
$\psi_{10} = \phi_3 - \phi_4 + 2\phi_{18}$
$\psi_{11} = \phi_5 - \phi_6 + 2\phi_{19}$
$\psi_{12} = \phi_7 - \phi_8 + 2\phi_{20}$
$\psi_{13} = \phi_9 - \phi_{10} + 2\phi_{21}$
$\psi_{14} = \phi_{11} - \phi_{12} + 2\phi_{22}$
$\psi_{15} = \phi_{13} - \phi_{14} + 2\phi_{23}$
$\psi_{16} = \phi_{15} - \phi_{16} + 2\phi_{24}$

the coefficients resemble (4.1.23). A tremendous conceptual simplification can be made when relationships between the c_i 's are examined. Equations (4.1.23) can be rewritten

$$\begin{aligned}
 c_1 &= 1 & c_5 &= c_1 c_2 c_3 \\
 c_2 &= -\alpha & c_6 &= c_1 c_2 c_4 \\
 c_3 &= -\beta & c_7 &= c_1 c_3 c_4 \\
 c_4 &= -\gamma & c_8 &= c_2 c_3 c_4
 \end{aligned} \tag{4.1.25}$$

Now a cusp-satisfying ψ_{CI} becomes

$$\begin{aligned}
 \psi_{CI} &= (a+c_2 a', \overline{b+c_3 b'}, c+c_4 c') \\
 &\quad + (b+c_3 b', \overline{a+c_2 a'}, c+c_4 c')
 \end{aligned} \tag{4.1.25a}$$

defining ψ_{CI} to a constant factor as a spin-projected different orbitals for different spins (DODS) wave function.^{*} Each orbital of the function (4.1.25) satisfies the orbital cusp condition, for example

$$p(k) (a(k) + c_2 a'(k)) \equiv 0 \tag{4.1.26}$$

Important generalizations follow immediately. Let the basis $\{\chi_i\}$ be replaced by appropriate linear

^{*} UHF functions are included in the group of DODS functions. Reasons for the present classification are given in Appendix B.

combinations, $\{\varphi_i\}$,

$$\varphi_i = \sum_j d_{ij} \chi_j \quad (4.1.27)$$

the standard form for analytical HF orbitals. A doublet, three-electron CI function can be formed from this basis:

$$\Psi_{CI} = \sum_i c_i \Psi_i, \quad (4.1.28)$$

where

$$\Psi_i = \begin{cases} (\varphi_\ell, \overline{\varphi}_m, \varphi_n) + (\varphi_m, \overline{\varphi}_\ell, \varphi_n) & \text{for } \Theta_1\text{-type terms} \\ (\varphi_\ell, \overline{\varphi}_m, \varphi_n) - (\varphi_m, \overline{\varphi}_\ell, \varphi_n) \\ \quad + 2(\varphi_\ell, \overline{\varphi}_n, \varphi_m) & \text{for } \Theta_2\text{-type terms} \end{cases}$$

and the c_i are linear variational coefficients. For

$\not p(k) \Psi_{CI} \equiv 0$ each orbital must satisfy the generalized orbital cusp condition

$$\not p(k) \varphi_i(k) \equiv 0$$

which holds either if $\not p \chi_i \equiv 0$ for the basis $\{\chi_i\}$ or if an appropriate linear constraint is applied to

φ_i . At least two of the χ_j in (4.1.27) should not satisfy $\not p \chi = 0$ if the linear constraint is to be possible, showing why equations (4.1.19), (4.1.22) can break down.

Finally, the spin cusp condition is a trivial consequence of the electron cusp condition. One can see from (4.1.15) that a spin cusp evaluation operator, $\not p(k) S_z(k)$, will give exactly the same restrictions on Ψ_{CI} as $p(k)$ since $S_z(k)$ will operate only on the spin, $S_\rho^m(k)$.

4.2 Applications to the lithium 2S groundstate

Expression (4.1.28) poses difficult computational problems because the orbitals φ_i must be variationally determined (with or without constraining) as well as Ψ_{CI} . Tractable procedures for calculating spin-optimized extended Hartree-Fock wave functions have been recently developed^{24,25}, making that method an attractive scheme to test the effectiveness of cusp constraints. The form of such functions resembles the Ψ_i in (4.1.28),

$$A [\varphi_1(1) \varphi_2(2) \varphi_3(3) (\theta_1 + k \theta_2)]$$

where k is variationally determined as in (4.1.24). Nuclear cusp constraints by the method of Weber and

Handy⁶⁹ or of Chong^{53*} can be applied to each ϕ_i . Weber, Handy and Parr⁶⁸ have already done this for Hartree-Fock functions, the primary reason being to decrease the number of linear parameters by satisfying a theoretical condition. But HF functions are not good enough, as discussed in Chapter I, to accurately predict spin densities, the object of this work. For technical reasons the spin-optimized EHF approach was discarded and all functions are cast in a CI format. This drastically limits the number of terms in the expansion (4.1.27) but has the advantages:

- (1) No SCF iterations on $\{\phi_i\}$ are necessary.
- (2) θ_1 , θ_2 spin terms are easily included.
- (3) Angular correlation can be added if desired while maintaining sharp \mathcal{L}^2 , \mathcal{L}_z .

Implementation of the last^{can} correspond to a generalization of the EHF method which has not been accomplished yet. Since simple wave functions are desired, expansion (4.1.26) will be restricted to two or three terms. The approach illustrated by cases 1 and 2 in 4.1 is utilized in this section. Orbitals like the one in (4.1.26) will be called cuspsatisfying orbitals (CSO) and will be designated

$$a(k) - \left(\frac{pa(k)}{pa'(k)} \right) a'(k) \equiv a - a' \equiv \underline{\underline{a - a'}} \quad (4.2.1)$$

* For atoms.

where $\rho\chi_{1s} = \sqrt{\frac{S_{1s}^3}{\pi}} (S_{1s} - Z)$, $\rho\chi_{2s} = \sqrt{\frac{S_{2s}^5}{3\pi}}$ and

$\rho\chi = 0$ for $\chi \neq \chi_{1s}, \chi_{2s}$. Thus (4.1.25a)

becomes

$$\begin{aligned}\psi_{CI} &= A [a-a'(1) \ b-b'(2) \ c-c'(3) \ \Theta_1] \\ &= (a-a', \overline{b-b'}, c-c') + (b-b', \overline{a-a'}, c-c')\end{aligned}\quad (4.2.2)$$

As before for cases 1 and 2, neither of the basis orbitals χ or χ' in $\underline{\chi-\chi'}$ must be individually cusp satisfying.

For exploratory purposes a simple CI wave function formed from the basis $\{\underline{\chi_i}\}$ was calculated. The function and its properties appear in Table XIII. Although it is much less extensive, this is the same type of basis used by Roothaan and coworkers^{65,66}, Goddard²⁵ and others. All exponents were partially optimized except $S_{1s} = Z$. Energy-wise the function is little better than HF-type functions (Table I). Such a basis makes cusp satisfaction trivial but there are disadvantages in this approach as applied to simple CI functions. First, expression of core polarization is difficult. The orbital making dominant contributions to the core is fixed. Second, χ_{2s} STO's are not allowed. Thus the 2s electronic function in lithium

Table XIII. Illustrative calculation: 3-term CI
function formed from $\{\underline{\chi}_i\}$ basis.

<u>STO basis:</u>	<u>orbital</u>	<u>exponent</u>
	χ_{1s}	3.0000
	χ_{3s}	3.1126
	χ_{3s}'	0.3000
	χ_{3s}''	0.9435

CI function:

$$\begin{aligned} \psi = & 0.77849(1s, \overline{1s}, 3s'') \\ & + 0.16375 [(1s, \overline{3s}, 3s'') + (3s, \overline{1s}, 3s'')] \\ & - 0.000339 [(1s, \overline{3s}', 3s'') + (3s', \overline{1s}, 3s'')] \end{aligned}$$

Properties:

-E	$Q^s(0)(\% \text{ error})$	$Q^e(0)(\% \text{ error})$	$\Gamma^e = \Gamma^s$
7.436183	0.1243(46.3)	13.6266(1.5)	-3.0000

must include several χ_{35} orbitals increasing the possibility of multiple energy minima.

Cusp-satisfying orbitals of the type $\underline{\chi - \chi'}$ are far more flexible. Any χ_{25} or χ_{15} with the stipulation $\zeta_{15} \neq Z$ is acceptable. The first functions studied had the form* (4.2.2)

$$\psi_i = \mathcal{A} [(\underline{\chi_{15} - \chi'_{15}})(\underline{\chi_{15}'' - \chi'_{15}''}) \underline{\phi_{25}}(\theta_1 + k\theta_2)] \quad (4.2.3)$$

where ϕ_{25} is
$$\left\{ \begin{array}{ll} \chi_{15}^{\text{IV}} - \chi_{15}^{\text{V}} & i=1 \\ \chi_{25} - \chi_{15}^{\text{IV}} & i=2 \\ \chi_{25} - \chi'_{25} & i=3 \end{array} \right\}.$$

k was either placed equal to zero or variationally determined (spin-optimized). The problem of exponent optimization was simplified by fitting each CSO into the (DODS) function

$$\psi' = (\chi_{15}, \overline{\chi'_{15}}, \chi_{25}) + (\chi_{15}', \overline{\chi_{15}}, \chi_{25}) \quad (4.2.4)$$

of Hurst et al³⁰ in the appropriate position and roughly optimizing its pair of exponents. The exponents thus obtained were placed in (4.2.3) and varied again to be sure a roughly minimum energy resulted.

* The notation is different from that in Chapter III.
 (1) Every orbital exponent can be different;
 ζ_{15} need not equal ζ_{25} .
 (2) Wave functions are not numbered according to the number of terms.

Exponents and properties are shown in Table XIV.

There are several points to note. Spin-optimization ($k \neq 0$ cases) is very important here as before. The maximum error in $Q^S(0)$ for the $k \neq 0$ cases is 4%. $Q^e(0)$ values are correct within 1%. These are very good numbers for such simple functions.

The best orbital exponents calculated for the function (4.2.4) by Hurst et al.³⁰ are $\zeta_{1s} = 3.298$, $\zeta'_{1s} = 2.068$, $\zeta_{2s} = 0.639$. The best ϕ_{1s} CSO's are seen to be just these orbitals with Dirac δ -like functions as corrections for the cusp, as a χ_{1s} orbital with an exponent as large as 13.0 or 20.0 is highly concentrated near the nucleus.

$$\chi_{1s} - \chi'_{1s} \equiv \chi_{1s} - \sqrt{\frac{\zeta_{1s}^3 (\zeta_{1s} - z)}{\zeta_{1s}^3 (\zeta'_{1s} - z)}} \chi'_{1s} \quad (4.2.5)$$

$$= \chi_{1s} - 0.001183 \chi'_{1s}$$

for $\zeta_{1s} = 3.3$, $\zeta'_{1s} = 20.0$. A corresponding δ -like correction for the ϕ_{2s} CSO could not be found. This is a very interesting result because Nesbet²⁷ (first entry in Table I) included χ_{1s} δ -type basis elements in his CI and HF functions without any apparent justification. As is evident in Table I he was not attempting to obtain a good energy, only a good spin density and chose his basis elements accordingly. The linear coefficients and configurations

Table XIV. Simple DODS wave functions* with CSO's.

Orbital Exponents								
STO Function	χ_{1s}	χ'_{1s}	χ''_{1s}	χ'''_{1s}	χ^{IV}_{1s}	χ^V_{1s}	χ_{2s}	χ'_{2s}
ψ_1	3.3	20.0	2.065	13.0	0.60	0.80	---	---
ψ_2	3.3	20.0	2.065	13.0	0.95	---	0.68	---
ψ_3	3.3	20.0	2.065	13.0	---	---	0.70	1.80

Properties					
Function		Energy	$Q^S(0)(\% \text{ error})$ (absolute)	$Q^e(0)(\% \text{ error})$ (absolute)	$\int e,s$
ψ_1	k=0	-7.445434	0.2174(6.0)	13.9626(.9)	-3.0000
	k \neq 0	-7.445435	0.2232(3.5)	13.9625(.9)	-3.0000
ψ_2	k=0	-7.445419	0.2160(6.6)	13.9614(.9)	-3.0000
	k \neq 0	-7.445420	0.2224(3.8)	13.9613(.9)	-3.0000
ψ_3	k=0	-7.445328	0.2265(2.1)	13.9553(.9)	-3.0000
	k \neq 0	-7.445329	0.2341(1.2)	13.9552(.9)	-3.0000
Hurst et al ^a	k=0	-7.4436	0.3002(29.8)	13.5193(2.3)	
Brigman and Matsen ^b	k \neq 0	-7.4436	0.2417(4.5)	13.5240(2.2)	
Best		-7.478069 ^c	0.2313 ^d (0.0)	13.8341 ^e (0.0)	-3.0000 ^f

* Functions are defined in equation (4.2.3).

^aFrom Table I, entry 6.

^bFrom Table I, entry 7.

^cReference [39].

^dReference [8].

^eReference [38].

^fTheoretical value.

of his functions are not listed in reference²⁷ so his cusp values could not be calculated.

These CSO's resemble Hulthén orbitals, described by Weare, Weber and Parr.⁶⁴ Compare the Os Hulthén orbital

$$O_{s\alpha\beta} = N_{os} [\exp(-\alpha r) - \exp(-\beta r)] \times \frac{1}{r}$$

with a ϕ_{1s} CSO

$$\underline{\chi_{1s} - \chi'_{1s}} = \chi_{1s} - \left(\frac{\cancel{\rho} \chi_{1s}}{\cancel{\rho} \chi'_{1s}} \right) \chi'_{1s} = N_{1s} \left[\exp(-sr) - \left(\frac{s-z}{s'-z} \right) \exp(-s'r) \right]$$

and a ϕ_{2s} CSO

$$\underline{\chi_{2s} - \chi'_{2s}} = \chi_{2s} - \left(\frac{\cancel{\rho} \chi_{2s}}{\cancel{\rho} \chi'_{2s}} \right) \chi'_{2s} = N_{2s} [\exp(-sr) - \exp(-s'r)] \times r.$$

Apparently only Os and lp Hulthén orbitals have been investigated but they give substantial improvements in energy over STO's.⁶⁴ Perhaps this explains the slight energy improvement of the CSO functions over those of Matsen and coworkers^{30, 32} shown in Table XIV for comparison.

Slightly more complicated wave functions were also investigated. An n orbital CSO, $\underline{\chi_1 - \chi_2 - \dots - \chi_n}$, can be incorporated into a CI function without formal

constraint procedures as follows. The orbital, ϕ , in

$$\mathcal{P}\phi = \mathcal{P} \sum_{i=1}^n c_i \chi_i \equiv 0 \quad (4.2.6)$$

can be expressed (to a normalization constant)

$$\phi = \sum_{i \neq j} c_i (\chi_i - \frac{\mathcal{P}\chi_i}{\mathcal{P}\chi_j} \chi_j) \quad , \text{ a sum of CSO's.}$$

The choice of χ_j is arbitrary. The case $n = 3$ for ϕ_{15} CSO's is demonstrated in Table XV for the function

$$\Psi_4 = \mathcal{A}[\phi_1 \phi_2 \phi_3 (\theta_1 + k\theta_2)],$$

$$\phi_1 = \underline{\underline{\chi_{15} - \chi_{15}''}} + c_1 \underline{\underline{\chi_{25}'' - \chi_{15}''}} \equiv \underline{\underline{\chi_{15} - \chi_{15}'' - \chi_{25}''}}$$

$$\phi_2 = \underline{\underline{\chi_{15}' - \chi_{15}'''}} + c_2 \underline{\underline{\chi_{25}''' - \chi_{15}'''}} \equiv \underline{\underline{\chi_{15}' - \chi_{15}''' - \chi_{25}'''}}$$

$$\phi_3 = \underline{\underline{\chi_{25} - \chi_{25}'}} \quad (4.2.7)$$

There are actually three independent linear coefficients (without the normalization factor) in the CI expansion instead of two for a legitimate DODS function because $c_3 = c_1 c_2$ is free to vary. δ -type corrections also exist in this function. Whether or not they would

- Table XV. (1) Ψ_4^* , a true CI function with two 3-orbital CSO's representing the core*.
- (2) Ψ_5^{**} , a spin-optimized CI function with p correlation in the core**.

Orbital Exponents

<u>STO</u> <u>Function</u>	χ_{1s}	χ_{1s}'	χ_{1s}''	χ_{1s}'''	χ_{2s}	χ_{2s}'	χ_{2s}''	χ_{2s}'''	$\chi_{2p,3p}$
Ψ_4	3.5	2.2	20.0	15.0	0.7	1.82	3.0	2.5	---
Ψ_5	3.3	24.0	2.065	14.0	0.7	1.8	---	---	5.0

Properties

Function	Energy	$Q^S(0)(\% \text{ error})$	$Q^e(0)(\% \text{ error})$	$\Gamma^{e,s}$
Ψ_4 k=0	-7.446249	0.2298(0.6)	13.8083(0.2)	-3.0000
Ψ_4 k \neq 0	-7.446276	0.2299(0.6)	13.8095(0.2)	-3.0000
Ψ_5 k \neq 0	-7.467491	0.2296(0.7)	13.9203(0.6)	-3.0000

* Ψ_4 is defined by equation (4.2.7).

** Ψ_5 is defined by equation (4.2.8).

be found with energy minimization subject to a constraint applied by Weber and Handy's method is unknown.

A CI function with p correlation, $\underline{\Psi}_5$, was constructed from $\underline{\Psi}_3$. If a configuration involving the product $\chi_{2p}\chi_{3p}$ had been included, $\underline{\Psi}_5$ would be a true DODS function.

$$\underline{\Psi}_5 = \mathcal{A} \left\{ [c_1 (\underline{\chi}_{15} - \chi'_{15}) \underline{\chi}_{15}'' - \chi'''_{15}) + c_2 (\chi_{2p})^2 + c_3 (\chi_{3p})^2] (\underline{\chi}_{25} - \chi'_{25}) [\theta_1 + k\theta_2] \right\} \quad (4.2.8)$$

For the $(\chi_{np})^2 \underline{\varphi}_{25}$ configurations $k = 0$ automatically. The restriction $\underline{J}_{2p} = J_{3p}$ simplified exponent optimization. Thus $\underline{\Psi}_5$ can be expanded as a four term CI function. Its exponents and properties are presented in Table XV. When compared with the entries in Table I it is seen to be a very good function indeed for its size.

With the exception of $\underline{\Psi}_4$ and $\underline{\Psi}_5$ all of these cusp-satisfying functions are true DODS functions. Self consistency is trivial for a two-orbital expansion with a linear constraint.

The success with CSO's may be fortuitous. To test this distinct possibility the stability of properties with respect to the δ -like corrections was examined for the spin-optimized ($k = 0$) $\underline{\Psi}_3$. Figure 6 shows a rough energy contour map as a function of J'_{15} and J'''_{15} . Figure 7 shows the same energy

Figure 6. Energy contour map of ψ_3 (Table XIV)
 Energy versus exponents ζ'_{1s} , ζ'''_{1s} of
 δ -type cusp correction orbitals.

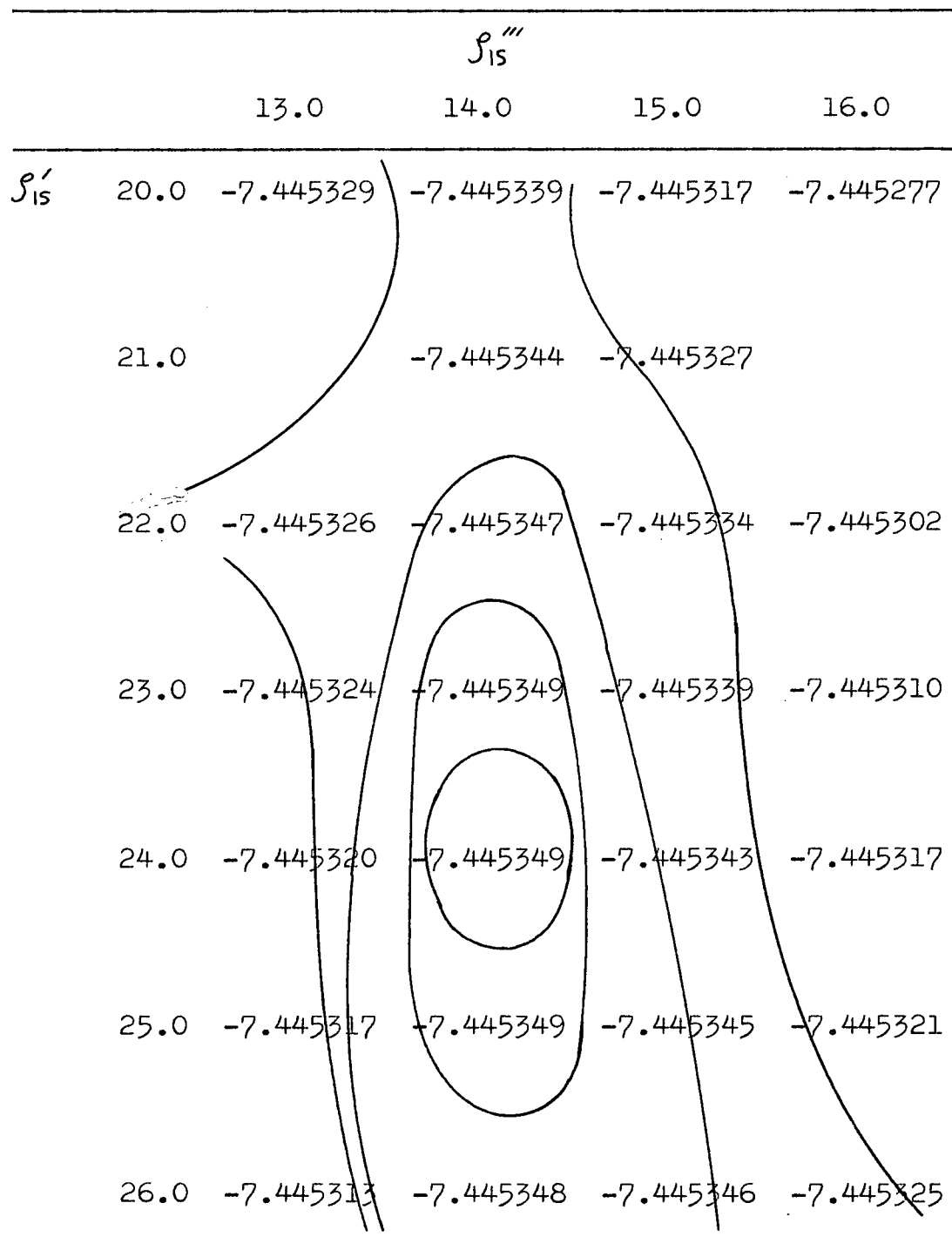


Figure 7. Properties of Ψ_3 (Table XIV) corresponding to energy contours in figure 6.

		\mathcal{J}_{1s}'''			
		13.0	14.0	15.0	16.0
\mathcal{J}_{1s}'	20.0	$Q^S = 0.2341$ $Q^e = 13.9552$	$Q^S = 0.2337$ $Q^e = 13.8858$	$Q^S = 0.2334$ $Q^e = 13.8273$	
	21.0		$Q^S = 0.2340$ $Q^e = 13.9028$	$Q^S = 0.2337$ $Q^e = 13.8442$	
	22.0	$Q^S = 0.2347$ $Q^e = 13.9875$	$Q^S = 0.2343$ $Q^e = 13.9180$	$Q^S = 0.2339$ $Q^e = 13.8594$	$Q^S = 0.2336$ $Q^e = 13.8093$
	23.0	$Q^S = 0.2349$ $Q^e = 14.0014$	$Q^S = 0.2345$ $Q^e = 13.9319$	$Q^S = 0.2342$ $Q^e = 13.8732$	
	24.0	$Q^S = 0.2352$ $Q^e = 14.0140$	$Q^S = 0.2348$ $Q^e = 13.9445$	$Q^S = 0.2344$ $Q^e = 13.8858$	
	25.0	$Q^S = 0.2354$ $Q^e = 14.0255$	$Q^S = 0.2350$ $Q^e = 13.9559$	$Q^S = 0.2346$ $Q^e = 13.8972$	$Q^S = 0.2343$ $Q^e = 13.8471$
	26.0	$Q^S = 0.2356$ $Q^e = 14.0361$	$Q^S = 0.2352$ $Q^e = 13.9665$	$Q^S = 0.2348$ $Q^e = 13.9078$	$Q^S = 0.2345$ $Q^e = 13.8576$

contours superimposed on the corresponding properties.

The sensitivity of properties to changes in S'_{1s} ,

S''_{1s} is seen to be small around the energy minimum.

The main energy contributions come from χ_{1s} , χ''_{1s}

STO's. Optimization with respect to S_{1s} , S''_{1s} is

more easily accomplished and a sensitivity study not

as essential. These figures answer the question, 'Can

any δ -type exponent be employed in a basis?'

Another test for CSO's lies in increasing the size of basis. Schaefer et al⁴¹ compare the basis dependence of $Q^S(0)$ for previously calculated SEHF functions of the first row elements, boron through fluorine, and conclude that a large basis ensures stability of properties.

Perhaps the present successes do not arise from satisfaction of the nuclear cusp condition. Recall that Nesbet's²⁷ results with δ -type functions are excellent also. A true CI wave function, Ψ'_3 (16 terms) was formed with the same basis as the cusp-satisfying function, Ψ_3 , but with free variation of all linear coefficients. A second true CI function, Ψ''_3 (4 terms) did not use the δ -type χ_{1s} cusp correction orbitals. The effects of these δ orbitals can be seen in Table XVI. Ψ_3 (Table XIV), of course, utilizes the δ orbitals and has the correct cusp.

Table XVI. True CI functions formed from STO basis listed in Table XIV.

CI Function	Corresponding CSO Function	Configurations	Spin Functions
ψ_3'	(with ' δ ' orbitals)	$\chi_{1s}\chi_{1s}''\chi_{2s}, \chi_{1s}\chi_{1s}''\chi_{2s}', \chi_{1s}\chi_{1s}'''\chi_{2s},$ $\chi_{1s}\chi_{1s}'''\chi_{2s}', \chi_{1s}\chi_{1s}''\chi_{2s}, \chi_{1s}\chi_{1s}''\chi_{2s}',$ $\chi_{1s}\chi_{1s}'''\chi_{2s}, \chi_{1s}\chi_{1s}'''\chi_{2s}'$	θ_1, θ_2
ψ_3''	' δ ' (without orbitals)	$\chi_{1s}\chi_{1s}''\chi_{2s}, \chi_{1s}\chi_{1s}''\chi_{2s}'$	θ_1, θ_2

Properties

Function	Energy	$Q^S(0)(\% \text{ error})$	$Q^e(0)(\% \text{ error})$	Γ^e	Γ^s
ψ_3'	-7.445560	0.2239(3.2)	13.9086(0.5)	-2.9249	-1.9217
ψ_3''	-7.444890	0.2416(4.4)	13.4671(2.7)	-2.8956	-3.1253

One must keep in mind that the function of Brigman and Matsen^{*} has a reasonable spin density (entry 7 in Table I) in the first place. Ψ_3'' closely duplicates their results as expected. Addition of δ -type orbitals to the basis improves $Q^S(0)$ considerably and in fact, Ψ_3' , with a very poor cusp, has properties similar to Ψ_3 . The progression from Ψ_3' (16 term CI) to Ψ_3 (2 term cusp-satisfying function), however, shows a 2.2% improvement of the error in $Q^S(0)$ at the expense of a tiny sacrifice in energy (2×10^{-4} a.u.). The better spin density of Ψ_3 is apparently due to cusp satisfaction.

Unfortunately it could be concluded from this study, taking into account the rather good spin densities of Ψ_3' and the function of Brigman and Matsen, that δ -type orbitals rather than correct cusp conditions might be responsible for the excellent results. Authors 5, 14, 15, 74 have criticized Nesbet²⁷ in varying degrees for including δ -type terms in his bases. This work does demonstrate that nuclear cusp conditions provide a theoretical avenue to Nesbet's approach even though they cannot yet be said to affect, to any great extent, the accuracy of calculated spin density. Further investigation will determine the generality of CSO's. The spin-optimized EHF methods of Goddard

* The function of Brigman and Matsen [32] is essentially the function of Hurst et al [30] with a triplet core spin term.

and Ladner²⁵, Kaldor and Harris²⁴ are ideal for such a study. Effects of exponent optimization, size of STO basis, inclusion of δ -type terms with and without nuclear cusp constraints, and extension of CSO's to larger systems should be examined.

4.3 Application to the lowest lithium 2P state

The method of two-orbital CSO's is now utilized to calculate $Q^S(0)$ for the lithium 2P state. A function similar to ψ_i , $i = 1, 2, 3$ for lithium 2S with CSO's,

$$\psi_{2p} = A [(\chi_{1s} - \chi_{1s}' \chi_{1s}'' - \chi_{1s}''') (\chi_{2p} + c_1 \chi_{3p}) (\theta_1 + k\theta_2)] \quad (4.3.1)$$

was partially optimized. δ -type cusp corrections were also found here, at minimum energy. Since χ_{np} trivially satisfies the nuclear cusp condition no constraint is needed to be applied to the orbital,

$\psi_{2p} = \chi_{2p} + c_1 \chi_{3p}$. The more general coalescence conditions (2.3.8a) could have determined c_1 . The function properties are compared with previously published results in Table XVII, ordered by energy. Whereas CSO's for lithium 2S groundstate give similar results to the spin-optimized calculations (compare the eleventh entry in Table I with properties listed in Table XIV),

Table XVII. Calculations on the lowest 2P state of lithium.

Description of wave functions	Reference	Energy	Spin density at the nucleus		Electron density at the nucleus	
			$Q^S(0)$	Reference	$Q^e(0)$	Reference
HF	42	-7.365069	0.00000	42	13.6534	42
UHF	42	-7.365076	-0.01747	42	13.6535	42
PUHF	42	-7.365080	-0.00582	42	13.6535	42
GF	42	-7.365091	-0.02304	42	13.6534	42
Spin-optimized DODS with CSO's	present ^{a,b}	-7.377569	-0.02234	present ^a	13.5501	present ^a
Spin-optimized EHF	24	-7.380087	-0.0169	24		
Spin-optimized EHF	25	-7.380116	-0.0172	25	13.7065	
208 -term CI	23	-7.40366				
45-term CI	67	-7.40838	-0.02222	75		
Experimental	67	-7.41016	-0.0181	10		

^a $f_{1s} = 3.27$, $f_{1s}'' = 2.08$, $f_{1s}' = 30.0$, $f_{1s}''' = 17.0$, $f_p = 0.526$ for the function defined in (4.3.1).
 $f^e = f^s = -3.0000$

^b Multiplication of exponents by the scale factor 1.00144 gives a function with properties $E = -7.377584$, $Q^S(0) = -0.02226$, $Q^e(0) = 13.6031$.

for lithium 2^2P there is a substantial difference. Goddard⁴² has cast doubt on the reliability of the experimental spin density. If the presently accepted experimental value is actually too low then the spin-optimized DODS function may be better than the spin-optimized EHF functions. On the other hand inclusion of correlation in the K shell orbitals will decrease the magnitude of the calculated (DODS) value somewhat. More work with a larger basis is definitely needed to assess the value of CSO's.

CHAPTER V

SUMMARY AND CONCLUDING REMARKS

The hypothesis that satisfaction of nuclear cusp conditions should lead to good point properties at the nucleus, was investigated for approximate wave functions by employing several different cusp constraints. Forcing necessary integral cusp conditions, although correcting the free variational electron density at the nucleus (as found by Chong and Yue for helium CI functions) invariably overcorrected to an extent that the magnitudes of error before and after constraint were similar. No generally applicable relationships between spin density at the nucleus and cusp constraints were found. The CI functions with Θ_2 -type spin terms studied had the property that if the free variational value of Γ^s was greater than $-Z$ some improvement occurred upon forcing $\Gamma^s = -Z$ while the opposite was true when Γ^s was less than $-Z$. Necessary weighting constraints did not appear to be useful for calculating $Q^{e,s}(0)$. But weighting with the free variational groundstate eigenvector closely

approximated traditional diagonal constraint results while utilizing the method of Weber and Handy⁶⁹ to avoid computational problems. For constraints that are not too severe, (the constrained function is almost equal to the free variational function), this weighting procedure should provide a good estimate of a true diagonal constraint with less effort.

Sufficient nuclear cusp constraints were applied to CI wave functions. The resulting form resembled analytical, spin-optimized, extended Hartree-Fock functions. Only a minuscule basis was employed, because the constraint functions were evaluated in configuration interaction form. The most important result was the appearance of Dirac δ -like orbitals correcting the cusp when energy was roughly minimized. Very good spin densities for the lithium 2S ground-state were calculated but further tests are necessary to determine if cusp satisfaction is responsible.

Questions to be answered include

- (1) Will a larger basis adversely effect $Q^S(0)$?
- (2) Will δ -like corrections, demonstrated by Nesbet²⁷ and by this work to improve $Q^S(0)$, appear when a larger basis is used?

Only studies with a larger basis in conjunction with the constrained variation methods of Weber and Handy

or Chong will indicate whether satisfaction of nuclear cusp conditions truly affect point properties at the nucleus.

A scheme for nuclear cusp conditions found in Table XVIII unifies the various approaches. The necessary and sufficient cusp condition is written

$$\rho(k) \Psi \equiv 0 \quad (5.1.1)$$

for any electron. The one-electron form of this condition dictates that individual electron orbitals in Ψ must satisfy the cusp condition.

The one-electron orbital basis can be composed of either single functions, $\{\chi_i\}$, or more generally, linear combinations of functions, $\{\phi_i\}$, $\phi_i = \sum_k d_{ik} \chi_k$. The former case leads to the basis $\{\underline{\chi}_i\}$, $\rho(k) \underline{\chi}(k) \equiv 0$, originally derived in a different manner by Roothaan and Kelly.⁶⁵ Very recently, Goddard⁷⁶ utilized this type of basis for analytical EHF atomic wave functions of boron through fluorine with the expressed purpose of improving $Q^S(0)$ values. He concluded that $Q^S(0)$ converged much faster (with respect to the size of the basis) with $\{\underline{\chi}_i\}$ than $\{\chi_i\}$. The drawbacks of this approach are large. No χ_{2s} orbital, or χ_{1s} with $J_{1s} \neq Z$ can be employed. Free variation of these

Table XVIII. Hierarchy of necessary and sufficient cusp conditions for atoms.^a

Wave function	Sufficient cc ^b	Necessary and Sufficient cc ^b	Necessary cc ^b
Exact, Φ		1) Kato ⁴⁷ 2) Pack and Byers Brown ² 3) $\nabla\Phi = 0^c$	Integral cusp conditions of Chong ⁶²
CI function without r_{ij} , Ψ	STO cusp-satisfying basis $\{\chi_i\}^c$	CSO's $\{\underline{\varphi}\}^c$	1) Integral cusp constraints of Chong ⁶² ^c 2) Weighted cusp constraints ^c
SCF one-electron orbital, ϕ	STO cusp-satisfying basis of Roothaan and Kelly ⁶⁵ , $\{\chi_i\}$	1) Integral cusp constraints of Chong ⁵³ 2) Cusp constraints of Weber, Handy and Parr ⁶⁸ 3) CSO's $\{\underline{\varphi}\}^c$	

^aNecessity and sufficiency refer to cusp conditions after wave function type is specified.

^bCusp conditions (cc).

^cThis work.

two orbitals should be important both for energy and description of the region about the nucleus. Goddard's conclusions do reinforce the idea behind this work.

The more general one-electron orbitals, $\{\varphi_i\}$, can be linearly constrained to satisfy sufficient and necessary cusp conditions. The resulting cusp-satisfying orbitals, $\{\underline{\varphi}_i\}$, are flexible and do not show the disadvantages of the set, $\{\underline{\chi}_i\}$.

The Pauli principle ensures that

$$\sum_k p(k) \Psi \equiv 0 \quad (5.1.2)$$

is also a necessary and sufficient condition. Thus the weighted cusp constraints are derived immediately by integration:

$$\langle f | \sum_k p(k) | \Psi \rangle \equiv 0 \quad (5.1.3)$$

These conditions are sufficient if they hold for each member of a complete set. The necessary cusp conditions are the special case,

$$f = \Psi$$

Integration destroys sufficiency because orbital overlaps contribute to the quantity $\langle f | \sum_k p(k) | \Psi \rangle$ rather than just $(p(k) \Psi)$.

There is a final comment on cusp and coalescence conditions. Experiments are being performed on positron-electron annihilations in molecules. One would expect effects from annihilation to be extremely dependent on the wave function at coalescence.⁷⁷ The usefulness and application of cusp constraints should still be examined with respect to this important new development.

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APPENDIX A

ATOMIC UNITS

A discussion of the significance and usefulness of atomic units (a.u.) is found in reference [78] . A recent tabulation of values of the fundamental constants appears in [79] . The basic a.u. are defined here in c.g.s. units.

Quantity	a.u.
mass	$1 = m_e = 9.1091 \times 10^{-28} \text{ g.}$
charge	$1 = e = 4.80298 \times 10^{-10} \text{ e.s.u.}$
length	$1 \text{ bohr} = a_0 = \frac{\hbar^2}{m_e e^2} = 5.29167 \times 10^{-9} \text{ cm.}$
angular momentum	$1 = \hbar = \frac{h}{2\pi} = 1.0544 \times 10^{-27} \text{ erg sec.}$
energy	$1 \text{ hartree} = \frac{e^2}{a_0} = 4.3594 \times 10^{-11} \text{ erg}$
magnetic moment	$1 \text{ bohr magneton} = \frac{e\hbar}{2m_e c} = 9.2732 \times 10^{-21} \frac{\text{erg}}{\text{Gauss}}$

For atomic (as opposed to molecular) calculations a different definition of mass is used:

$$1 = \mu = \frac{m_e M}{m_e + M} \text{ where } M \text{ is the mass of the}$$

nucleus. The a.u. for length, energy, etc. are re-defined

$$a = \frac{\hbar^2}{\mu e^2} = \text{mass corrected bohr}$$

$$\frac{e^2}{a} = \text{mass corrected hartree.}$$

APPENDIX B

SOME IMPORTANT TYPES OF APPROXIMATE
ATOMIC WAVE FUNCTIONS

First a remark on the symmetry of atomic wave functions. The non-relativistic Hamiltonian for an atom commutes with S^2 , L^2 , S_z , L_z , the total spin and orbital angular momenta and their z components respectively. An exact wave function, therefore, has sharp values for these observables and it seems proper that approximate wave functions should too. Because electrons are fermions, the Pauli principle holds also. The antisymmetrization operator, A , will designate this symmetry.

The most widely used approximation in atomic and molecular physics is the Hartree-Fock (HF) method arrived at by considering each electron to be in an average potential field created by all other electrons. This results directly in a single particle interpretation for the approximate function where an electron cannot experience direct interactions with the others. The HF function is the very best, with energy as a criterion, antisymmetrized product of one-electron

spin orbitals:

$$\Psi_{HF} = \mathcal{A} [\prod_i \psi_i(r_i, s_i)]$$

The ψ_i may be expanded in a complete set of one-electron functions. If this expansion is truncated for practical applications, an analytical HF approximation to the true HF function results.

There are a number of restrictions¹⁷ that must be made on the most general HF orbitals so that the function will be an eigenfunction of S^2 , L^2 ,

S_z , L_z :

- (1) The spin orbital, ψ_i , should be separable into spin and orbital components.

$$\psi_i(r, s) = \phi_i(r) \nu_i(s), \quad \nu_i = \alpha, \beta$$

The more general (unrestricted) case is

$$\psi_i(r, s) = \phi_i^\alpha(r) \alpha(i) + \phi_i^\beta(r) \beta(i)$$

- (2) The orbital should be separable into radial and angular components.*

$$\phi(r, \theta, \phi) = U_i(r) Y_i(\theta, \phi)$$

* The present discussion applies to atoms only.

- (3) If (2) is true, $\mathcal{U}_i(r)$ should be independent of m_ℓ .^{*}
- (4) If (1) is true, $\mathcal{U}_i(r)$ should be independent of m_s .^{*}

Closed-shell systems present no problems. All the above restrictions automatically hold and the resulting best function is called the restricted Hartree-Fock (RHF) or (usually) just the HF function. Open-shell systems having an unpaired spin exhibit core polarization only if (4) is lifted. This is called the unrestricted Hartree-Fock (UHF) approximation, ambiguously since only one restriction has been lifted. It is also referred to as a spin-polarized Hartree-Fock. Releasing of the restrictions (2), (3) has not been investigated to any extent.

Sharpness of \mathcal{S}^2 , \mathcal{L}^2 , \mathcal{S}_z , \mathcal{L}_z can be restored to unrestricted functions by the appropriate projection operator(s). The projected unrestricted Hartree-Fock (PUHF) is thus obtained by projecting a (minimized) UHF function to have sharp \mathcal{S}^2 . Spin projection before minimization is physically more realistic, resulting in the extended Hartree-Fock (EHF), also referred to as spin-polarized projected Hartree-Fock or spin extended Hartree-Fock (SEHF).

*The present discussion applies to atoms only.

Such projected functions are no longer true HF functions since they contain more than one determinant, but they have an independent particle interpretation if they are calculated with averaged Coulomb potentials.

The independent particle interpretation of the HF method, although leading to conceptual advantages, also provides serious shortcomings. Electrons are permitted by the functional form of the HF function to come too close together. The Pauli principle automatically provides a 'Fermi hole' for correlating the movement of two electrons with parallel spins--the (determinantal) wave function can vanish identically. The 'correlation hole' or 'Coulomb hole' describing the instantaneous interactions between two electrons of different spins does not exist in HF functions.

The method of different orbitals for different spins (DODS) improves on the HF procedure by allowing electrons having different spins (and thus not affected by the Pauli principle) to occupy different spatial positions. To be an eigenfunction of \mathcal{S}^2 a DODS function is usually spin projected. The term, DODS, is collective, including all UHF, EHF, etc. (except RHF) functions but implying a degree of approximation below that of analytical HF derived functions. For

example if

$$\Psi_{SEHF} = A P(\varphi_{1s}\alpha \varphi'_{1s}\beta \varphi_{2s}\alpha)$$

where P is a spin projection operator, the orbitals φ are expanded in the same one-electron basis, usually relatively large,

$$\varphi_{1s} = \sum a_i \chi_i, \quad \varphi'_{1s} = \sum b_i \chi_i, \text{ etc.}$$

whereas for

$$\Psi_{DODS} = A P(\varphi_{1s}\alpha \varphi'_{1s}\beta \varphi_{2s}\alpha)$$

the orbitals φ are expanded in a small basis--so that their resemblance to accurate analytical HF-type orbitals is in notation only--that can be different for each orbital.

$$\varphi_{1s} = \chi_1, \quad \varphi'_{1s} = \chi_2, \text{ etc.}$$

A remark on open and closed shells can be made here.

'Open shell' can refer to an atom like lithium with an unfilled outer shell or it can refer to a split shell described by the DODS method. Helium for example

has a closed K shell but a DODS description is an open shell description. Entries 6, 7, 8, 9 in Table I could be more accurately labelled as functions having split K shells.

There are two main types of functions containing correlation: a configuration interaction (CI) function (a kind of generalization of the DODS method), and a correlated function (sometimes referred to as a Hylleraas-type function). Both, of necessity, depart from the independent particle picture. A CI function consists of a sum of antisymmetrized products of one-electron spin orbitals.

$$\Psi_{CI} = A \sum_i a_i \prod_k (\varphi_k^i(r_k) \chi_k(s_k))$$

A complete one-electron basis with all possible products can describe an exact function. In practice

Ψ_{CI} is truncated and the $\{a_i\}$ determined by the usual secular equations. If a full basis (in the sense that all combinations of any particular truncated set of

φ_i 's, with all possible l , m , s quantum numbers, are present) is used, Ψ_{CI} is automatically an eigenfunction of S^2 , L^2 , S_z , L_z . Or determinants may be grouped to individually be eigenfunctions of these operators (the examples in the text). Any complete set of one-electron functions will generate

a CI function, Gaussian orbitals, Slater-type orbitals (STO's), Laguerre polynomials, etc. STO's provide a physically realistic basis. The CI approach suffers from slow convergence and the growing number of important configurations with the number of particles.

Correlated wave functions contain interelectronic coordinates, r_{ij} , explicitly and so are not expanded in a one-electron basis set. Such a function for 2S lithium atom could appear^{6, 80}

$$\Psi = A \left[\sum \varphi_{ijk\ell mn} (C_{ijk\ell mn}^{(1)} \Theta_1 + C_{ijk\ell mn}^{(2)} \Theta_2) \right]$$

The Θ_i terms are the two linearly independent spin doublet functions for three electrons, and the c 's are variationally determined linear coefficients.

A form for the φ 's is

$$\varphi_{ijk\ell mn} = r_1^i r_2^j r_3^k r_{23}^\ell r_{13}^m r_{12}^n \exp(-\alpha r_1 - \beta r_2 - \gamma r_3)$$

Factors like $\frac{r_{ij}}{r_i + r_j}$, $\frac{r_i - r_j}{r_{ij}}$ could be included as

well. Disadvantages of this method are:

- (1) The number of possible φ 's increases tremendously with the number of electrons.
- (2) The necessary integrals can be complicated to evaluate.

APPENDIX C

CONSTRAINED VARIATION

C.1 Introduction

Constrained variation is a technique that builds selected information, either of a theoretical or empirical nature, into a variationally determined approximate wave function. The purpose is the anticipated improvement over the free variational function in related expectation values. Basically the problem is the minimization of energy of a trial function while forcing it to have predetermined properties. Since the procedure removes degrees of freedom in the variational coefficients of the trial function it results in an energy sacrifice, ΔE , from the energy of a free variational function.

The idea of constrained variation was first introduced by Mukherji and Karplus⁸¹ and basic theory was developed by Rasiel and Whitman⁸² and Byers Brown.⁷⁰ Initial successes in applications^{81, 82, 83} have led to refinements^{69, 71, 72, 73} and further applications. 3, 4, 59, 84, 85 Methods of solving constrained secular equations are now presented.

C.2 Single constraints

The energy of a trial function Ψ ,

$$E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle \quad (\text{C.2.1})$$

is to be minimized subject to a constraint

$$\langle \Psi | M | \Psi \rangle / \langle \Psi | \Psi \rangle = \mu \quad (\text{C.2.2})$$

conveniently expressed

$$\begin{aligned} C &= \langle C \rangle = 0 , \\ C &= M - \mu . \end{aligned} \quad (\text{C.2.3})$$

M can be any observable or attribute not commuting with H . The modified variational principle becomes

$$\delta E + \lambda \delta C = 0$$

or more explicitly

$$\langle \delta \Psi | \{ H - E + \lambda C \} | \Psi \rangle = 0 \quad (\text{C.2.4})$$

The determination of the Lagrange multiplier, λ , constitutes the major problem in applying constraints.

The form of (C.2.4) restricts \mathcal{G} to be an Hermitian operator. Byers Brown⁷⁰ has developed the most extensive treatment of constrained variation by considering λ as a perturbation parameter. In this perturbation approach the energy in (C.2.4) is designated as E_{fict} , a fictitious energy and is expanded in a power series

$$E_{\text{fict}} = \sum_{n=0}^{\infty} \lambda^n E^{(n)} \quad (\text{C.2.5})$$

where $E^{(i)}$ is the i^{th} order perturbation energy. Since $E_{\text{fict}}(\lambda) = \langle H + \lambda \mathcal{G} \rangle$,

$\frac{\partial E_{\text{fict}}}{\partial \lambda} = \langle \mathcal{G} \rangle = C(\lambda)$ by the Hellmann-Feynman theorem. When the constraint (C.2.3) is satisfied, $\lambda = \lambda_{\text{opt}}$, the optimum value of λ . Because

$$C(\lambda) = \sum_{n=1}^{\infty} \lambda^{n-1} n E^{(n)}, \quad (\text{C.2.6})$$

$$\left(\frac{\partial E_{\text{fict}}}{\partial \lambda} \right)_{\lambda=\lambda_{\text{opt}}} = \sum_{n=1}^{\infty} \lambda_{\text{opt}}^{n-1} n E^{(n)} = 0. \quad (\text{C.2.7})$$

The series (C.2.5) must converge rapidly if a perturbation approach is to be of value and can be truncated after 'k' terms. The $E^{(i)}$ are readily evaluated for the Rayleigh-Schrödinger perturbation expansion and a value

for λ_{opt} can be obtained by inverting the power series (C.2.7)

$$\lambda_{\text{opt}} \approx \lambda_0 = \sum_n a_n \left(\frac{-E^{(1)}}{2 E^{(2)}} \right)^n \quad (\text{C.2.8})$$

Properties can be evaluated by a double perturbation approach, or directly from the wave function satisfying

$$\langle \delta \Psi | \{ H - E + \lambda_0 \mathcal{C} \} | \Psi \rangle = 0 \quad (\text{C.2.9})$$

The closeness of the approximation, $\lambda_{\text{opt}} \approx \lambda_0$, depends on the convergence of the inverted series and the truncation errors involved.

The parametrization approach⁷¹ avoids the question of convergence occurring in the perturbation approach. It is simple to apply; (C.2.4) is repeatedly solved for different values of λ until $C(\lambda_{\text{opt}}) = 0$ is found. The problem here is that a good initial guess for λ_{opt} is difficult. If one is fortunate enough to closely estimate λ_{opt} , it may be obtained to high accuracy by successive linear interpolations or extrapolations of $C(\lambda)$.

Chong⁷² has developed a perturbation-iteration approach by incorporating parametrization into the perturbation approach. $C(\lambda)$ is expanded in a Taylor

series about an estimate λ_n . For $\lambda_{n+1} = \lambda_n + \chi$

$$C(\lambda_{n+1}) = C(\lambda_n) + \sum_{n'=1}^k \chi^{n'} D_{n'}(\lambda_n) \quad (C.2.10)$$

where $D_{n'}(\lambda_n) = \sum_{m=n'}^k \binom{m}{n'} \lambda_n^{m-n'} (m+1) E^{m+1}$

$\binom{m}{n'}$ are the binomial coefficients. Equation (C.2.8) provides an initial guess, λ_0 .

$C(\lambda_n) = \langle \Psi(\lambda_n) | G | \Psi(\lambda_n) \rangle / \langle \Psi(\lambda_n) | \Psi(\lambda_n) \rangle$ is evaluated with the solution to (C.2.9) for λ_n . Since $\lambda_{n+1} = \lambda_{\text{opt}}$ is desired $C(\lambda_{n+1})$ is set to zero and inversion of the truncated series (C.2.10) gives an estimate for χ . Usually a very few iterations suffice to give λ_{opt} to desired accuracy.

C.3 Multiple constraints

Byers Brown⁷⁰ extended his perturbation approach to include multiple constraints. The variation principle is

$$\delta E + \sum \lambda_i \delta C_i = 0 \quad (C.3.1)$$

Resulting series expansions and inversions are not easily worked out and thus his extension is not too practical.

Chong and Benston⁷³ observed approximate linear relationships in double constraints. The constraint conditions

$$\langle \mathcal{G}_1 \rangle = C_1(\lambda_{\text{opt}}, \eta_{\text{opt}}) = 0$$

$$\langle \mathcal{G}_2 \rangle = C_2(\lambda_{\text{opt}}, \eta_{\text{opt}}) = 0, \quad (\text{C.3.2})$$

λ , η the two Lagrange multipliers, are closely estimated by solving

$$C_1(\lambda, \eta) = A_{10} + A_{11}\lambda + A_{12}\eta$$

$$C_2(\lambda, \eta) = A_{20} + A_{21}\lambda + A_{22}\eta \quad (\text{C.3.3})$$

for $C_1 = C_2 = 0$ at $\lambda = \lambda_{\text{opt}}$, $\eta = \eta_{\text{opt}}$.

The coefficients $\{A_{ij}\}$ can be initially determined from the expectation values of \mathcal{G}_1 , and \mathcal{G}_2 for the free variational and singly constrained eigenfunctions,

$$C_1(0, 0) = A_{10} = \langle \mathcal{G}_1 \rangle \quad (\text{free variational})$$

$$C_2(0, 0) = A_{20} = \langle \mathcal{G}_2 \rangle \quad "$$

$$C_1(\lambda'_{\text{opt}}, 0) = A_{10} + A_{11}\lambda'_{\text{opt}} = 0$$

$$C_2(\lambda'_{\text{opt}}, 0) = A_{20} + A_{21}\lambda'_{\text{opt}}$$

$$C_1(0, \eta'_{\text{opt}}) = A_{10} + A_{12}\eta'_{\text{opt}}$$

$$C_2(0, \eta'_{\text{opt}}) = A_{20} + A_{22}\eta'_{\text{opt}} = 0 \quad (\text{C.3.4})$$

where $\lambda'_{opt}, \eta'_{opt}$ are optimum single constraint values.
The secular equation

$$\langle \delta \Psi | \{ H - E + \lambda G_1 + \eta G_2 \} | \Psi \rangle = 0$$

is solved using $\lambda_{opt}, \eta_{opt}$ from (C.3.3). Accurate evaluations of $C_1(\lambda_{opt}, \eta_{opt}), C_2(\lambda_{opt}, \eta_{opt})$ are made enabling the set of points (C.3.4) to be improved. Iteration proceeds until (C.3.2) holds. Usually only one or two cycles are needed.

An alternative to this approach is successive parametrization. The best λ for some value of η is found so that $C_1(\lambda^{best}, \eta) = 0$. λ is fixed and a new η is found giving $C_2(\lambda, \eta^{best}) = 0$. The process is repeated until self-consistency is achieved. Loeb and Rasiel⁸⁶ have employed this method. The disadvantage is that matrix eigenfunctions must be found at each step in the parametrization while equations (C.3.2) are simple, linear, algebraic equations.

C.4 Off-diagonal constraints

All methods discussed so far have been diagonal,

$$\langle \Psi | G | \Psi \rangle = 0 .$$

An off-diagonal constraint

$$\langle \psi | \mathcal{C} | \psi \rangle = 0 \quad , \quad \psi \neq \bar{\psi} \quad (\text{C.4.1})$$

can be imposed by defining a new pseudo-diagonal constraint operator⁸⁴

$$\mathcal{C}' = \mathcal{C} |\psi\rangle\langle\psi| + |\psi\rangle\langle\bar{\psi}| \mathcal{C} . \quad (\text{C.4.2})$$

The constraint condition (C.4.1) becomes

$$C' = \langle \psi | \mathcal{C}' | \psi \rangle = 0 \quad (\text{C.4.3})$$

where $\bar{\psi}$ is fixed and ψ is variationally determined. Self-consistency is achieved by reforming \mathcal{C}' after every calculation of ψ .

C.5 Off-diagonal linear constrained variation of Weber and Handy

No iteration or parametrization is necessary in this one-step approach. Multiple constraints are handled easily. The presentation of Weber and Handy⁶⁹ is followed.

Define the constrained wave function

$$\bar{\psi} = \sum C_K \psi_K$$

represented by the column vector, \mathbb{C} , in some orthonormal basis set $\{\psi_k\}$. Weber and Handy considered the constraint conditions

$$p_i^+ \mathbb{C} = 0 \quad , \quad i=1, \dots, m \quad (\text{C.5.1})$$

where each p_i defines a constraint. The set $\{p_i\}$ can be orthogonalized to $\{\hat{p}_i\}$ where

$$\hat{p}_i^+ \hat{p}_k = \delta_{ik} \quad (\text{C.5.2})$$

The resulting constrained secular equations are

$$(\mathbb{H} - \epsilon \mathbb{I}) \mathbb{C} = -\frac{1}{2} \sum_{i=1}^m \lambda_i \hat{p}_i \quad (\text{C.5.3})$$

\mathbb{I} is the unit matrix, \mathbb{H} is the Hamiltonian matrix in the basis $\{\psi_k\}$, and ϵ is the (constrained) energy of ψ . The beauty of the method lies in the elimination of the Lagrange multipliers, λ_k . Multiplying (C.5.3) by \hat{p}_k^+ one obtains

$$-\frac{1}{2} \lambda_k = \hat{p}_k^+ \mathbb{H} \mathbb{C} \quad (\text{C.5.4})$$

These values for the λ 's are substituted into (C.5.3) which is then manipulated into the set of secular equations

$$(B - \epsilon I) \mathcal{C} = 0 \quad (C.5.5)$$

where $B = (I - A) H (I - A)$, an Hermitian matrix and $A = \sum_k \hat{p}_k \hat{p}_k^+$. When B is diagonalized, m extraneous roots, ϵ_i , appear because m degrees of freedom are absorbed in the constraints. Weber and Handy show that these m roots all have value zero. Off-diagonal constrained variation is thus reduced to orthogonalization of the set $\{\hat{p}_k\}$ and solution of (C.5.5).

APPENDIX D

INTEGRAL CALCULATION

D.1 Primitive integrals for Slater-type orbitals
(STO's)

A general STO has the form

$$\chi_{nlm}(r, \theta, \phi) = \sqrt{\frac{(2s)^{2n+1}}{(2n)!}} r^{n-1} e^{-sr} Y_{lm}(\theta, \phi) \quad (\text{D.1.1})$$

The Y_{lm} 's are the usual spherical harmonics. Primitive integrals are those arising between one-electron basis functions. In energy calculations the following primitive integrals occur for atoms:

overlap integrals, $S_{ij} = \int \chi_i^*(\underline{r}) \chi_j(\underline{r}) d\tau$

kinetic energy integrals, $-\frac{1}{2} \int \chi_i^*(\underline{r}) \nabla^2 \chi_j(\underline{r}) d\tau$

nuclear attraction integrals, $Z \int \chi_i^*(\underline{r}) \frac{1}{r} \chi_j(\underline{r}) d\tau$

Coulomb and exchange integrals $\int \chi_i^*(\underline{r}_1) \chi_j^*(\underline{r}_2) \frac{1}{r_{12}} \chi_k(\underline{r}_1) \chi_l(\underline{r}_2) d\tau_1 d\tau_2$

Analytical formulae are given by Roothaan.⁸⁷

For cusp calculations the following primitive integrals arise:

$$\begin{array}{ll} \text{electron density} & Q_{ij} = \int \chi_i^*(\mathbf{r}) \frac{\delta(\mathbf{r})}{4\pi r^2} \chi_j(\mathbf{r}) d\mathbf{r} \\ \text{at the nucleus,} & \end{array}$$

$$\begin{array}{ll} \text{gradient at the} & G_{ij} = \int \chi_i^*(\mathbf{r}) \frac{\delta(\mathbf{r})}{4\pi r^2} \frac{\partial}{\partial \mathbf{r}} \chi_j(\mathbf{r}) d\mathbf{r} \\ \text{nucleus,} & \end{array}$$

Formulae are easily derived for these integrals from the definition of STO's (D.1.1):

$$Q_{ij} = \begin{cases} \frac{\sqrt{s_i^3 s_j^3}}{\pi} & , \text{ for } \chi_i, \chi_j \text{ both } \chi_{1s} \text{ orbitals} \\ 0 & , \text{ if } \chi_i, \chi_j \text{ are not both } \chi_{1s} \text{ orbitals} \end{cases}$$

$$G_{ij} = \begin{cases} \frac{-s_j \sqrt{s_i^3 s_j^3}}{\pi} & , \text{ if } \chi_i, \chi_j \text{ are } \chi_{1s} \text{ orbitals} \\ \frac{+s_j \sqrt{s_i^3 s_j^3}}{\sqrt{3} \pi} & , \text{ if } \chi_i \text{ is a } \chi_{2s} \text{ orbital and } \chi_j \text{ is a } \chi_{1s} \text{ orbital} \\ 0 & , \text{ for all other combinations of orbitals} \end{cases}$$

The spherical averaging operator defined in the text has not been shown, but it ensures that all p, d, f, \dots orbitals ($\ell > 0$) give a zero contribution to the cusp.

D.2 Collection of primitive integrals

The integrals directly employed in atomic calculations are those between Slater determinants $\{\phi_i\}$ where

$$\phi_i = \mathcal{A} \left[\prod_k (\chi_k^i \nu_k^i) \right] \quad (\text{D.2.1})$$

\mathcal{A} is the antisymmetrization operator, $\{\chi\}$ are STO's and ν_k are spin functions α , β . The general method of handling these is given by Slater.⁸⁸ For three electron functions with $S = 1/2 = S_z$ a simplified approach can be used. If general primitive integrals are designated

$$f_{ij} = \int \chi_i^*(k) F(k) \chi_j(k) d\tau_k$$

the Slater determinants (D.2.1) may be compactly written

$$\phi_i = (a(1)\alpha(1), b(2)\beta(2), c(3)\alpha(3))$$

$$\phi_j = (e(1)\alpha(1), f(2)\beta(2), g(3)\alpha(3)) \quad , \text{ etc.}$$

Then

$$\begin{aligned}
F_{ij} &= \langle \phi_i | \sum_{k=1}^3 \mathcal{F}(k) | \phi_j \rangle \\
&= \langle a(1)\alpha(1) b(2)\beta(2) c(3)\alpha(3) | \sum_{k=1}^3 \mathcal{F}(k) | \{ e(1)\alpha(1) f(2)\beta(2) g(3)\alpha(3) \\
&\quad + f(1)\beta(1) g(2)\alpha(2) e(3)\alpha(3) + g(1)\alpha(1) e(2)\alpha(2) f(3)\beta(3) \\
&\quad - f(1)\beta(1) e(2)\alpha(2) g(3)\alpha(3) - e(1)\alpha(1) g(2)\alpha(2) f(3)\beta(3) \\
&\quad - g(1)\alpha(1) f(2)\beta(2) e(3)\alpha(3) \} \rangle.
\end{aligned}$$

If $\mathcal{F}(k)$ is spinless the spins may be integrated out immediately.

$$\begin{aligned}
F_{ij} &= \langle a(1) b(2) c(3) | \sum_{k=1}^3 \mathcal{F}(k) | e(1) f(2) g(3) - g(1) f(2) e(3) \rangle \\
&= f_{ae} S_{bf} S_{cg} + S_{ae} f_{bf} S_{cg} + S_{ae} S_{bf} f_{cg} \\
&\quad - f_{ag} S_{bf} S_{ce} - S_{ag} f_{bf} S_{ce} - S_{ag} S_{bf} f_{ce}
\end{aligned}$$

in terms of primitive overlap and \mathcal{F} integrals.

If $\sum_k \mathcal{F}(k)$ contains spin--for example, the spin density operator, $\sum_i \frac{\delta(r_i)}{4\pi r_i^2} \mathcal{S}_z(i)$ --the spin functions may be operated on and then integrated out in an analogous way.

Further integral collections, between eigenfunctions of \mathcal{L}^2 , etc., as used in the text, are trivial, consisting of linear combinations of the integrals between Slater determinants.

APPENDIX E

DESCRIPTIONS AND PROPERTIES OF THE
WAVE FUNCTIONS $\bar{\Phi}_{10}$ THROUGH $\bar{\Phi}_{18}$

The Slater-type orbital basis for this series is defined in Table V, as are the configurations in $\bar{\Phi}_{10}$, the key wave function. The significance of $\bar{\Phi}_{14a}$ is explained in the text following equation (3.3.4). The notation, $\{\bar{\Phi}_i\}$, used below, means the entire collection of configurations making up the CI function, $\bar{\Phi}_i$. Properties of $\bar{\Phi}_{10}$ through $\bar{\Phi}_{18}$ are listed in Table XIX. The functions $\bar{\Phi}_{11}$ through $\bar{\Phi}_{18}$ have the configurations

$$\begin{aligned}
 \bar{\Phi}_{11}: & \{\bar{\Phi}_{10}\}, 1515'25''\theta_2 \\
 \bar{\Phi}_{12}: & \{\bar{\Phi}_{11}\}, 1525'25''\theta_2 \\
 \bar{\Phi}_{13}: & \{\bar{\Phi}_{12}\}, 2515'25''\theta_2 \\
 \bar{\Phi}_{14}: & \{\bar{\Phi}_{13}\}, 2525'25''\theta_2 \\
 \bar{\Phi}_{15}: & \{\bar{\Phi}_{14}\}, 1515'35''\theta_2 \\
 \bar{\Phi}_{16}: & \{\bar{\Phi}_{15}\}, 1525'35''\theta_2 \\
 \bar{\Phi}_{17}: & \{\bar{\Phi}_{16}\}, 2515'35''\theta_2 \\
 \bar{\Phi}_{18}: & \{\bar{\Phi}_{17}\}, 2525'35''\theta_2
 \end{aligned}$$

$$\bar{\Phi}_{14a}: \{\bar{\Phi}_{10}\}, 1515'25''\theta_2, 1525'25''\theta_2, 1515'35''\theta_2, 1525'35''\theta_2$$

Table XIX. Free variational and constrained properties of the wave functions Φ_{10} through Φ_{14}

Function	Constraint	-Energy	$Q^s(0)$	$Q^e(0)$	Γ^e	Γ^s	ΔE	λ
Φ_{10}	None	7.467389	0.2677	13.7522	-2.9732	-3.2795	---	0.0
	$\Gamma^e = \gamma$	7.467254	0.2753	13.9191	-3.0000	-3.2973	0.000135	$+0.579772 \times 10^{-4}$
	$\Gamma^s = \gamma$	7.465334	0.1715	13.5519	-2.9447	-3.0000	0.002055	-0.521667×10^{-2}
	$\Gamma^e = \Gamma^s = \gamma$	7.464736	0.1686	13.8901	-3.0000	-3.0000	0.002653	$\lambda^e = +0.125277 \times 10^{-3}$ $\lambda^s = -0.585347 \times 10^{-2}$
Φ_{11}	None	7.467408	0.2244	13.7538	-2.9737	-3.1545	---	0.0
	$\Gamma^e = \gamma$	7.467278	0.2265	13.9179	-3.0000	-3.1587	0.000130	$+0.569242 \times 10^{-4}$
	$\Gamma^s = \gamma$	7.467394	0.1867	13.7524	-2.9736	-3.0000	0.000014	-0.621749×10^{-4}
	$\Gamma^e = \Gamma^s = \gamma$	7.467264	0.1879	13.9168	-3.0000	-3.0000	0.000144	$\lambda^e = +0.569979 \times 10^{-4}$ $\lambda^s = -0.615931 \times 10^{-4}$
Φ_{12}	None	7.467418	0.2148	13.7512	-2.9730	-2.9487	---	0.0
	$\Gamma^e = \gamma$	7.467283	0.2197	13.9189	-3.0000	-3.0193	0.000136	$+0.578992 \times 10^{-4}$
	$\Gamma^s = \gamma$	7.467418	0.2201	13.7518	-2.9731	-3.0000	0.0	$+0.608938 \times 10^{-5}$
	$\Gamma^e = \Gamma^s = \gamma$	7.467282	0.2177	13.9190	-3.0000	-3.0000	0.000137	$\lambda^e = +0.579931 \times 10^{-4}$ $\lambda^s = -0.227478 \times 10^{-5}$
Φ_{13}	None	7.467424	0.2048	13.7515	-2.9731	-2.7800	---	0.0
	$\Gamma^e = \gamma$	7.467289	0.2088	13.9189	-3.0000	-2.8446	0.000135	$+0.5776325 \times 10^{-4}$
	$\Gamma^s = \gamma$	7.467420	0.2229	13.7527	-2.9733	-3.0000	0.000004	$+0.144304 \times 10^{-4}$
	$\Gamma^e = \Gamma^s = \gamma$	7.467287	0.2219	13.9187	-3.0000	-3.0000	0.000137	$\lambda^e = +0.574015 \times 10^{-4}$ $\lambda^s = +0.100169 \times 10^{-4}$
Φ_{14}	None	7.467429	0.2135	13.7500	-2.9728	-2.9790	---	0.0
	$\Gamma^e = \gamma$	7.467291	0.2153	13.9192	-3.0000	-2.9870	0.000138	$+0.582329 \times 10^{-4}$
	$\Gamma^s = \gamma$	7.467429	0.2150	13.7500	-2.9728	-3.0000	0.0	$+0.891716 \times 10^{-6}$
	$\Gamma^e = \Gamma^s = \gamma$	7.467291	0.2163	13.9192	-3.0000	-3.0000	0.000138	$\lambda^e = +0.582305 \times 10^{-4}$ $\lambda^s = +0.534754 \times 10^{-6}$

Table XIX (continued)

Function Constraint		-Energy	$Q^S(0)$	$Q^E(0)$	Γ^E	Γ^S	ΔE	λ
Φ_{15}	None	7.467483	0.2269	13.7529	-2.9736	-3.0271	---	0.0
	$\Gamma^E = \gamma$	7.467354	0.2297	13.9168	-3.0000	-3.0380	0.000129	$+0.563295 \times 10^{-4}$
	$\Gamma^S = \gamma$	7.467483	0.2248	13.7529	-2.9736	-3.0000	0.0	-0.121657×10^{-5}
	$\Gamma^E = \Gamma^S = \gamma$	7.467354	0.2268	13.9168	-3.0000	-3.0000	0.000129	$\lambda^E = +0.563403 \times 10^{-4}$ $\lambda^S = -0.166013 \times 10^{-5}$
Φ_{16}	None	7.467490	0.2289	13.7510	-2.9730	-3.0622	---	0.0
	$\Gamma^E = \gamma$	7.467356	0.2310	13.9176	-3.0000	-3.0596	0.000134	$+0.570254 \times 10^{-4}$
	$\Gamma^S = \gamma$	7.467490	0.2241	13.7509	-2.9731	-3.0000	0.0	-0.278766×10^{-5}
	$\Gamma^E = \Gamma^S = \gamma$	7.467356	0.2264	13.9176	-3.0000	-3.0000	0.000134	$\lambda^E = +0.570195 \times 10^{-4}$ $\lambda^S = -0.258561 \times 10^{-5}$
Φ_{17}	None	7.467492	0.2298	13.7511	-2.9731	-3.0754	---	0.0
	$\Gamma^E = \gamma$	7.467359	0.2320	13.9176	-3.0000	-3.0741	0.000133	$+0.569446 \times 10^{-4}$
	$\Gamma^S = \gamma$	7.467491	0.2240	13.7511	-2.9731	-3.0000	0.000001	-0.337136×10^{-5}
	$\Gamma^E = \Gamma^S = \gamma$	7.467358	0.2263	13.9176	-3.0000	-3.0000	0.000134	$\lambda^E = +0.569374 \times 10^{-4}$ $\lambda^S = -0.320967 \times 10^{-5}$
Φ_{18}	None	7.467495	0.2287	13.7501	-2.9729	-3.0542	---	0.0
	$\Gamma^E = \gamma$	7.467360	0.2312	13.9178	-3.0000	-3.0590	0.000135	$+0.572685 \times 10^{-4}$
	$\Gamma^S = \gamma$	7.467495	0.2246	13.7501	-2.9729	-3.0000	0.0	-0.239282×10^{-5}
	$\Gamma^E = \Gamma^S = \gamma$	7.467360	0.2267	13.9178	-3.0000	-3.0000	0.000135	$\lambda^E = +0.572745 \times 10^{-4}$ $\lambda^S = -0.252666 \times 10^{-5}$
Φ_{19a}	None	7.467479	0.2304	13.7521	-2.9733	-3.0394	---	0.0
	$\Gamma^E = \gamma$	7.467348	0.2360	13.9172	-3.0000	-3.0988	0.000131	$+0.566694 \times 10^{-4}$
	$\Gamma^S = \gamma$	7.467479	0.2260	13.7517	-2.9732	-3.0000	0.0	-0.487691×10^{-5}

Larsson's
100 term
correlated
function, see
entry 18 in Table I