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Self-Consistent-Field Theory for One-Positron Many-Electron Systems*

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A theory for the structure of one-positron many-electron atoms and molecules in bound states is presented. The purpose of the theory is to permit the accurate calculation of positron lifetimes, angular correlation for two-photon annihilation, and accurate positron binding energies, but not necessarily quantities which depend upon purely electronic correlation. We therefore use a modified orbital approximation for the electrons, the modification consisting of the introduction of explicit electron-positron correlation into each electronic orbital. The kinetic energies of the electrons and positron are treated on the same footing, and the Born-Oppenheimer approximation is applied to the nuclei. No spin-dependent or relativistic terms are included in the Hamiltonian. In this paper we treat only those systems for which the electrons constitute a closed shell, and we do not consider the spatial symmetry of the atom or molecule.

I. INTRODUCTION

There is ample experimental evidence indicating that bound positron-atom and positron-molecule complexes play an important role in annihilation in gases and in molecular liquids and solids.[1] Unfortunately, it is presently impossible to quantitatively interpret experimental results in terms of the structure of such complexes, owing to the lack of a suitable theory. Of equal importance is the converse: Experimental results cannot now be used to deduce structural features of the parent complexes. The purpose of this paper is to provide the necessary theory, at least for a certain class of systems.

Our approach is, first, to calculate a wave function for the complex of interest using ordinary Schrödinger nonrelativistic wave mechanics, and second, to use the wave function so obtained to calculate the annihilation parameters. This procedure originated with Shirokov[2] and Chang Lee[3] and corresponds to using first-order perturbation theory to estimate the coupling between photon and matter fields.

The method for calculating wave functions accounts accurately for those effects which are critical in estimating annihilation parameters, and makes suitable approximations for those which are not. Specifically, if there are n electrons, we assume that the $n-1$ nonannihilating electrons are merely inert spectators during the annihilation event and do not begin to relax into eigenstates of the residual system until after annihilation is complete. Chang Lee[3] and others have shown that this is a good approximation, under which the annihilation rate and two-photon angular correlation are one-electron properties. Such properties are usually accounted for within 2–5% accuracy by Hartree-Fock wave functions. Expressions for evaluating the annihilation parameters in terms of such wave functions have been given for systems in which the electrons constitute a closed shell by Ferrell[4] and Chang Lee.[3] In the present work we consider only such systems and such wave functions. We so limit ourselves in order to focus our attention on the practical problem: how to get sufficiently accurate annihilation parameters from the simplest possible approximate wave functions. A treatment of a more general class of systems (i.e., open electronic shell) will be given later. Many important positron complexes have closed electronic shells: positronium chloride, positron-water, positron-chlorobenzene, positronium hydride, etc.

In Chang Lee's approximation, annihilation depends upon the coalescence of annihilating particles, and hence, in order to yield an accurate annihilation rate, an approximate wave function of a complex must be accurate in regions of space where the positron is close to an electron. Furthermore, since the Hamiltonian heavily weights regions of space near coalescence of annihilating particles, wave-function accuracy there is important also for energies – specifically, positron and positronium binding energies of atoms and molecules. Theoretical work on solids by many workers suggests that calculated angular correlation curves may not depend critically on positron-electron correlation, as does the annihilation rate.

Making an approximate wave function reflect short-range two-particle correlation accurately can be viewed as building the proper interparticle cusp into the wave function. In the main, there are two methods for accomplishing this: a direct method in which one explicitly puts into the wave function the interparticle radial coordinate $|\vec{r}_a - \vec{r}_b|$ for the two particles a and b in whose relative motion one is interested; and an indirect method in which a reference point c (usually a third particle) is chosen and the coordinates $|\vec{r}_a - \vec{r}_c|$, $|\vec{r}_b - \vec{r}_c|$, and $\angle acb$ are included in the wave function and given a special interdependence to approximate the cusp. In the direct method one can accurately satisfy the cusp condition in a simple way, whereas in the indirect method a lengthy expansion of the wave function in a basis set is required even to approximate the correct coalescence behavior. Despite the large expansion, the indirect method always requires less labor.

For example, a large number of studies of electronic correlation in the helium atom show that in an expansion of the wave function in a basis set the correct short-range interelectronic behavior is established with far fewer terms by the direct method (using the Hylleraas coordinates s, t, and u) than by the indirect method (configuration interaction). In this case, extension of the direct method, even to atoms with only three and four electrons, has led to very complicated integrals, whereas the indirect method while less accurate is easily extended to much more complicated atoms. A related observation can be made concerning molecules by comparing a wave function comprised of one-center configurations (indirect method) with a wave function built up from orbitals centered at each nucleus (direct method). In this case, the two particles, whose short-range correlation we consider, are an electron and a nucleus other than the one which serves as the origin of the one-center wave function. For wave functions of comparable compactness (a compact wave function has a short expansion in a basis), the direct method gives a much more accurate wave function near such nuclei, but requires much more labor.

The relevance of these remarks for the present study is that we may choose either method for representing short-range electron-positron correlation in systems of interest, and our choice will be guided by the conflict between convenience of calculations and accuracy of the results. Except for very simple systems, all previous work on positron-atom and positron-molecule complexes has been done using the indirect method. The purpose of the present work is to show how the direct method can be applied to the positron-electron correlation problem in many-electron systems.

Our approach is simple and direct: To make up the over-all wave function for the complex we multiply a one-positron spin-and-space function times a Slater determinant of one-electron spin-and-space functions. Each of the electronic spin orbitals is generalized by making it depend also on the position of the positron. In this way the crucial electron-positron correlation is accounted for satisfactorily, thus presumably leading to acceptable accuracy in calculated annihilation parameters. The purpose of the positronic orbital is to ensure that the correct positronic charge density is given by the wave function, and to provide a convenient means to properly account for the symmetry of the point group of the molecule.

In Sec. II we set up the necessary symbolism, and in Sec. III the self-consistent-field (SCF) equations are derived and presented as differential equations. Section IV is a discussion of how to solve the equations, including the Roothaan expansion method and perturbation approaches. Section V reviews previous work on positron-atom and positron-molecule complexes with reference to the approach presented here.

All previous calculations of one-positron, many-electron systems (more than two) have suffered from at least one of the following deficiencies: Positron-electron correlation has been ignored; the Pauli exclusion principle for the electrons has been violated; symmetry considerations involving spin angular momentum or electron interchange have been incorrectly treated. The present approach correctly accounts for all of these, and may have significant implications for calculations on scattering systems and solids as well as the class of systems we consider here, bound finite systems.

II. PRELIMINARY DEFINITIONS

For systems in which the electrons form closed shells we take as our approximate wave function

$$\Psi = \psi_p(\vec{x}_p) A \prod_\mu \psi_\mu(\vec{x}_\mu, \vec{r}_p), \tag{2.1}$$

where A is the electronic antisymmetrizer and normalizer, and ψ denotes spin-orbitals of the particles designated by the subscripts (p means positron and μ means electron). The argument $\vec{x}$ denotes spin (σ) and space ($\vec{r}$) variables of the particle indicated by the subscript. We call ψ_μ an electronic spin-orbital even though it depends also on the position of the positron. We choose the ψ's to be eigenfunctions of the one-particle spin operators:

$$\psi_p(\vec{x}_p) = \phi_p(\vec{r}_p)\,[\alpha(p) \text{ or } \beta(p)]\;, \tag{2.2}$$

$$\psi_\mu(\vec{x}_\mu, \vec{r}_p) = \phi_i(\vec{r}_\mu, \vec{r}_p)\,\alpha(\mu) = \phi_i^\mu \alpha_u ,$$

$$\text{for } \mu = 2i - 1 \tag{2.3}$$

$$\psi_\mu(\vec{x}_\mu, \vec{r}_p) = \phi_i(\vec{r}_\mu, \vec{r}_p)\beta(\mu) = \phi_i^\mu \beta_\mu ,$$

$$\text{for } \mu = 2i .$$

Thus, each electronic orbital ϕ_i is doubly occupied, the electron spins are paired, and Ψ satisfies the Pauli principle for the electrons.

This form for Ψ is, aside from the $\vec{r}_p$ dependence of the electronic orbitals, precisely that of Hartree-Fock theory as far as the electrons are concerned, and it is very general from the point of view of the positron. Indeed, it is not unique since, for example, ϕ_p can be included as a factor in any of the ψ_μ. Therefore, we still have considerable freedom to incorporate desired features into the wave function. In particular, the $\vec{r}_p$ dependence of each electronic orbital ϕ_i can be exploited to insert electron-positron correlation directly into the wave function through the coordinate $r_{\mu p} = |\vec{r}_\mu - \vec{r}_p|$. In this way Ψ can be made to satisfy all the electron-positron cusp conditions exactly by requiring each ϕ_i to satisfy[5]

$$\left(\frac{\partial \phi_i}{\partial r_{\mu p}}\right)\Bigg|_{r_{\mu p} = 0} = \tfrac{1}{2}\phi_i(r_{\mu p} = 0) . \tag{2.4}$$

This may be a convenient way to cultivate accuracy in a trial wave function in regions of many-particle space which correspond to coalescence of annihilating pairs.

If we thus use the $\vec{r}_p$ dependence of ϕ_i to express only the short-range correlation of the motions of the annihilating particles, then the gross distribution of positronic charge in the molecule is manifested through the positronic orbital ϕ_p. In this case each ϕ_i can be made to belong to an irreducible representation of the symmetry group of the complex. Then $A\Pi_\mu \psi_\mu$ is totally symmetrical, and the symmetry of Ψ is just the symmetry of ψ_p.

In the summations that appear below, a Greek running index (not α) indicates an n-fold sum over electrons or spin orbitals, a Roman running index indicates an $\frac{1}{2}n$-fold sum over orbitals, and a sum α means a sum over nuclei.

Integrations over space and sums over spin are indicated by angular brackets:

$$\langle\psi_p|\theta|\psi_p\rangle = \sum(\sigma_p)\int d\vec{r}_p\, \psi_p^*(\vec{x}_p)\theta\psi_p(\vec{x}_p) ,$$
$$\langle\psi_\mu|\theta'|\psi_\nu\rangle = \sum(\sigma_\mu)\int d\vec{r}_\mu\, \psi_\mu^*(\vec{x}_\mu, \vec{r}_p)\theta'\psi_\nu(\vec{x}_\mu, \vec{r}_p), \tag{2.5}$$

where θ and θ' are arbitrary operators. Spatial integrations alone are indicated by parentheses:

$$(\phi_p|\theta|\phi_p) = \int d\vec{r}_p\, \phi_p^*(\vec{r}_p)\theta\phi_p(\vec{r}_p) ,$$
$$(\phi_i|\theta'|\phi_j) = \int d\vec{r}_\mu \phi_i^*(\vec{r}_\mu, \vec{r}_p)\theta'\phi_j(\vec{r}_\mu, \vec{r}_p). \tag{2.6}$$

Without loss of generality, we require the orbitals to obey

$$(\phi_i|\phi_j) = \delta_{ij}, \tag{2.7a}$$

$$(\phi_p|\phi_p) = 1 . \tag{2.7b}$$

The Hamiltonian which we consider here is, in familiar atomic units,[6]

$$H = \sum_\mu h_\mu + \sum_{\mu<\nu}\sum g_{\mu\nu} + h_p + \sum_\mu g_{\mu p} ,$$
$$h_\mu = -\tfrac{1}{2}\nabla_\mu^2 - \sum_\alpha \frac{Z_\alpha}{r_{\mu\alpha}} ,$$
$$h_p = -\tfrac{1}{2}\nabla_p^2 + \sum_\alpha \frac{Z_\alpha}{r_{p\alpha}}, \tag{2.8}$$
$$g_{\mu\nu} = 1/r_{\mu\nu} ,$$
$$g_{\mu p} = -1/r_{\mu p} .$$

Using this notation the annihilation rate for two-photon production, $\tau_{2\gamma}^{-1}$, is given by Chang Lee[3] (in atomic units)

$$\tau_{2\gamma}^{-1} = 2\pi\alpha^3 \sum_i \int d\vec{r}\, |\phi_p(\vec{r})\phi_i(\vec{r}, \vec{r})|^2 , \tag{2.9}$$

where α is the fine-structure constant and the units of $\tau_{2\gamma}$ are atomic units of time (2.4189×10^{-17} sec). Likewise, the amplitude for 2γ annihilation with the photons having total momentum $\vec{k}$ is

$$\Gamma(\vec{k}) = [\alpha^3/(2\pi)^2]\sum_i \left|\int d\vec{r}\, \phi_p(\vec{r})\phi_i(\vec{r}, \vec{r})e^{i\vec{k}\cdot\vec{r}}\right|^2, \tag{2.10}$$

and the quantity usually observed in the measurement of 2-photon angular correlation is

$$\gamma(k_z) = \int dk_x \int dk_y\, \Gamma(\vec{k}) . \tag{2.11}$$

The rate and amplitude are related by

$$\tau_{2\gamma}^{-1} = \int d\vec{k}\, \Gamma(\vec{k}) = \int dk_z\, \gamma(k_z) . \tag{2.12}$$

Clearly the rate and amplitude can be expressed as expectation values of one-electron operators:

$$\tau_{2\gamma}^{-1} = \langle\Psi|\Delta_1|\Psi\rangle, \quad \Delta_1 = \pi\alpha^3\sum_\mu \delta(\vec{r}_\mu - \vec{r}_p) , \tag{2.13}$$

and

$$\Gamma(\vec{k}) = \langle\Psi|\Delta_2|\Psi\rangle, \tag{2.14a}$$

$$\Delta_2 = \frac{\alpha^3}{2(2\pi)^2} \sum_\mu \left| e^{-i\vec{k}\cdot\frac{1}{2}(\vec{r}_\mu+\vec{r}_p)} \delta(\vec{r}_\mu - \vec{r}_p)\right)$$

$$\times \left(e^{-i\vec{k}\cdot\frac{1}{2}(\vec{r}_\mu+\vec{r}_p)} \delta(\vec{r}_\mu - \vec{r}_p) \right| , \qquad (2.14b)$$

where the parentheses in Eq. (2.14b) imply integration over $\vec{r}_\mu$ and $\vec{r}_p$. We emphasize that Eqs. (2.13)–(2.14b) are valid only for systems for which the wave function has the form (2.1).

III. SCF EQUATIONS

A. Variational Expression

The expectation values of the various terms in the Hamiltonian are easily seen to be

$$\langle\Psi | \sum_\mu h_\mu | \Psi\rangle = (\phi_p | 2\sum_i (\phi_i | h_\mu | \phi_i) | \phi_p) , \qquad (3.1)$$

$$\langle\Psi | \sum_{\mu<\nu}\sum g_{\mu\nu} | \Psi\rangle = (\phi_p | \sum_i \sum_j (\phi_i | 2J_j - K_j | \phi_i) | \phi_p), \qquad (3.2)$$

where we have slightly generalized a familiar set of definitions:

$$J_j = (\phi_j^\nu | g_{\mu\nu} | \phi_j^\nu) = \int d\vec{r}_\nu \frac{|\phi_j(\vec{r}_\nu, \vec{r}_p)|^2}{|\vec{r}_\mu - \vec{r}_\nu|}$$

$$= J_j(\vec{r}_\mu, \vec{r}_p) , \qquad (3.3)$$

$$K_j = \phi_j^\mu (\phi_j^\nu | g_{\mu\nu} ;$$

$$K_j F(\vec{r}_\mu, \vec{r}_\nu, \vec{r}_p) = \phi_j(\vec{r}_\mu, \vec{r}_p) \int d\vec{r}_\nu \qquad (3.4)$$

$$\times \frac{\phi_j^*(\vec{r}_\nu, \vec{r}_p) F(\vec{r}_\nu, \vec{r}_\mu, \vec{r}_p)}{|\vec{r}_\mu - \vec{r}_\nu|} ,$$

where F is an arbitrary scalar function of the indicated variables. Continuing,

$$\langle\Psi | \sum_\mu g_{\mu p} | \Psi\rangle = (\phi_p | 2\sum_i (\phi_i | g_{\mu p} | \phi_i) | \phi_p) , \qquad (3.5)$$

$$\left\langle\Psi \left| \sum_\alpha \frac{Z_\alpha}{r_{p\alpha}} \right| \Psi\right\rangle = \left(\phi_p \left| \sum_\alpha \frac{Z_\alpha}{r_{p\alpha}} \right| \phi_p\right); \qquad (3.6)$$

and finally,

$$\langle\Psi | -\tfrac{1}{2}\nabla_p^2 | \Psi\rangle = \langle\psi_p | \langle \det \Pi_\mu \psi_\mu | -\tfrac{1}{2}\nabla_p^2 | \Pi_\mu \psi_\mu\rangle | \psi_p\rangle . \qquad (3.7)$$

We have separately expressed the results for the two parts of h_p since one part is very simple but the other requires a little more treatment. The positronic Laplacian in Eq. (3.7) is understood to operate on the $(n+1)$-fold product $\psi_p \Pi_\mu \psi_\mu$. In detail,

$$\nabla_p^2(\psi_p \Pi_\mu \psi_\mu) = (\nabla_p^2 \psi_p)(\Pi_\mu \psi_\mu) + \psi_p \sum_\mu (\nabla_p^2 \psi_\mu) \prod_{\nu\neq\mu} \psi_\nu + 2(\nabla_p \psi_p) \cdot \sum_\mu (\nabla_p \psi_\mu) \prod_{\lambda\neq\mu} \psi_\nu + 2\psi_p \sum_{\mu<\nu}\sum (\nabla_p \psi_\mu) \cdot (\nabla_p \psi_\nu) \prod_{\lambda\neq\mu,\nu} \psi_\lambda , \qquad (3.8)$$

where now and hereafter the differential operators are understood to operate only on the single function immediately following. For example, $\nabla_p^2 | \phi_i) \times | \phi_p)$ means $\phi_p(\nabla_p^2 \phi_i)$, not $\nabla_p^2(\phi_i \phi_p)$; and $\nabla_p | \phi_i) | \phi_p)$ means $\phi_p(\nabla_p \phi_i)$, not $\nabla_p(\phi_i \phi_p)$.

The rather large collection of terms in (3.8) arises of course because of the $\vec{r}_p$ dependence of each electronic spin orbital. This dependence is a major source of difficulty in working out numerical solutions in our approach, but only by accurately accounting for positron-induced distortions in the electronic spin orbitals can we hope to achieve acceptable accuracy in calculating lifetimes and positron and positronium affinities of complex atoms and molecules.

The kinetic energy of the positron is now seen to be

$$\langle\Psi | -\tfrac{1}{2}\nabla_p^2 | \Psi\rangle = (\phi_p | -\tfrac{1}{2}\nabla_p^2 - \sum_i (\phi_i | \nabla_p^2 | \phi_i)$$

$$+ 2\sum_i \vec{A}_i \cdot \nabla_p + \sum_i \sum_j (\phi_i | 2\vec{A}_j$$

$$- \vec{B}_j | \cdot \nabla_p \phi_i) | \phi_p) , \qquad (3.9)$$

where $\vec{A}_j = -(\phi_j | \nabla_p | \phi_j) = \vec{A}_j(\vec{r}_p) \qquad (3.10)$

and

$$\vec{B}_j = -\nabla_p \phi_j (\phi_j | ;$$

$$\vec{B}_j \cdot \vec{F}(\vec{r}_\mu, \vec{r}_\nu, \vec{r}_p) = -[\nabla_p \phi_j(\vec{r}_\mu, \vec{r}_p)] \cdot \int d\vec{r}_\nu \qquad (3.11)$$

$$\times \phi_j^*(\vec{r}_\nu, \vec{r}_p) \vec{F}(\vec{r}_\nu, \vec{r}_\mu, \vec{r}_p) ,$$

where $\vec{F}$ is an arbitrary vector function of the indicated variables.

For an important class of orbitals the $\vec{A}_i$ quantities are zero. The condition for $\vec{A}_i$ being zero is deduced by differentiating Eq. (2.7a) with respect to $\vec{r}_p$:

$$(\nabla_p^* \phi_i | \phi_j) + (\phi_i | \nabla_p | \phi_j) = 0 . \qquad (3.12)$$

Setting $i=j$, we have $\vec{A}_i = -\vec{A}_i^*$. But $\vec{A}_i$ and $\vec{A}_i^*$ are identical if their respective integrands are equal,

$$\phi_i \nabla_p \phi_i^* = \phi_i^* \nabla_p \phi_i \quad . \tag{3.13}$$

Therefore, whenever Eq. (3.13) holds, $\vec{A}_i$ is identically zero. Equation (3.13) holds if ϕ_i is real, and for much less restrictive conditions also. For example, if all the $\vec{r}_p$ dependence of $\phi_i(\vec{r}_\mu, \vec{r}_p)$ can be expressed as a real factor of ϕ_i,

$$\phi_i(\vec{r}_\mu, \vec{r}_p) = U_i(\vec{r}_\mu)\chi(\vec{r}_\mu, \vec{r}_p), \quad \chi \text{ real} \quad , \tag{3.14}$$

then Eq. (3.13) holds. In the remainder, we assume that Eq. (3.13) holds.

The total energy $E = \langle \Psi | H | \Psi \rangle$ which we now vary is thus the sum of the right hand sides of Eqs. (3.1), (3.2), (3.5), (3.6), and (3.9):

$$E = \big(\phi_p \big| h_p + 2\textstyle\sum_i (\phi_i | h_\mu + g_{\mu p} - \frac{1}{2}\nabla_p^2 | \phi_i) + \textstyle\sum_i \sum_j (\phi_i | 2J_j - K_j - \vec{B}_j \cdot \nabla_p | \phi_i) \big| \phi_p \big) \quad . \tag{3.15}$$

The variation in E is achieved by allowing ϕ_p^* and ϕ_i^* to take on constrained variations independently of ϕ_p and ϕ_i. The constraints, which we now impose with Lagrange multipliers, are those which ensure orthonormality among the electronic functions and the normality of ϕ_p: We want Eqs. (2.7) to be obeyed throughout the variation. The second constraint (2.7b) is imposed simply by adding to the expression $-\lambda_p[(\phi_p | \phi_p) - 1]$, where λ_p is a Lagrange multiplier. The first constraint (2.7a) we impose by adding

$$-\big(\phi_p \big| 2\textstyle\sum_i \sum_j \lambda_{ij} [(\phi_i | \phi_j) - \delta_{ij}] \big| \phi_p \big) \quad . \tag{3.16}$$

The Lagrange multipliers λ_{ij} are necessarily functions of $\vec{r}_p$, since we are applying a constraint on a function of $\vec{r}_p$ everywhere in positron-space. We assume that the λ_{ij} are independent of ϕ_p^*.

The variational functional J we now exhibit in full:

$$J = -\lambda_p[(\phi_p | \phi_p) - 1] - \big(\phi_p \big| 2\textstyle\sum_i \sum_j \lambda_{ij} [(\phi_i | \phi_j) - \delta_{ij}] \big| \phi_p \big) + \big(\phi_p \big| h_p + 2\textstyle\sum_i (\phi_i | h_\mu + g_{\mu p} - \frac{1}{2}\nabla_p^2 | \phi_i) + \textstyle\sum_i \sum_j (\phi_i | 2J_j - K_j - \vec{B}_j \cdot \nabla_p | \phi_i) \big| \phi_p \big) \quad . \tag{3.17}$$

B. Positronic Equation

We now vary ϕ_p^* in the above and set the result equal to zero in accordance with the variational principle. The resulting Euler-Lagrange equation is easily seen to be

$$(H_p - E)\phi_p = 0 \quad , \tag{3.18}$$

where we have identified the Lagrange multiplier λ_p as the total energy E [Eq. (3.15)] and where H_p, the effective Hamiltonian for the positron, is

$$H_p = h_p + \textstyle\sum_i \big(\phi_i \big| 2(h_\mu + g_{\mu p} - \frac{1}{2}\nabla_p^2) + \textstyle\sum_j (2J_j - K_j - \vec{B}_j \cdot \nabla_p) \big| \phi_i \big) \quad . \tag{3.19}$$

H_p may be partitioned into a purely positronic part h_p, a purely electronic part

$$V_e(\vec{r}_p) = \textstyle\sum_i \big(\phi_i \big| 2h_\mu + \textstyle\sum_j (2J_j - K_j) \big| \phi_i \big) \quad , \tag{3.20}$$

and a mixed part

$$X(\vec{r}_p) = \textstyle\sum_i \big(\phi_i \big| 2(g_{\mu p} - \frac{1}{2}\nabla_p^2) - \textstyle\sum_j \vec{B}_j \cdot \nabla_p \big| \phi_i \big) \quad . \tag{3.21}$$

V_e and X enter Eq. (3.18) as contributions to the effective potential seen by the positron, and X may be viewed as an interaction between the positron and the electrons. In addition to the obvious Coulomb interaction $2\sum_i (\phi_i | g_{\mu p} | \phi_i)$, X also contains

$$\tau_p = 2\textstyle\sum_i (\phi_i | -\frac{1}{2}\nabla_p^2 - \frac{1}{2}\textstyle\sum_j \vec{B}_j \cdot \nabla_p | \phi) \quad . \tag{3.22}$$

This term together with $-\frac{1}{2}\nabla_p^2$ in h_p embodies the effects of the positron kinetic energy operator, which enters in a complicated way because we have made each electronic orbital depend on the position of the positron. τ_p itself is associated with the kinetic effect on the positronic orbital of the distortion of each electronic orbital in two-particle (electron, positron) space. In addition to the direct (i.e., one-electron) part of τ_p,

$$2\textstyle\sum_i (\phi_i | -\frac{1}{2}\nabla_p^2 | \phi_i) \quad , \tag{3.23}$$

there is also an interelectronic kinetic coupling through the indirect part

$$-\textstyle\sum_i \sum_j (\phi_i | \vec{B}_j \cdot \nabla_p | \phi_i) \quad . \tag{3.24}$$

This is a genuine two-electron interaction which arises from the last term on the right of Eq. (3.8) and is the effect of correlating the motions of electron pairs through the positron. Since the effect involves three light bodies, we expect it to be unimportant compared to other terms in H_p. It is probably a small but significant part of the total electron correlation energy. A similar term arises also in the treatment of purely electronic molecules when effects of nuclear motion on electronic behavior are considered.

We note that the diagonal term in the double sum in (3.24), being $|\vec{A}_j|^2$, vanishes.

It is instructive to cast Eq. (3.18) in a form such that the eigenvalue is the binding energy of the positron. E itself is a large (negative) number of which the positron binding energy is a small fraction. The major part of E is the energy of the electrons, which can be written as $(\phi_p|V_e|\phi_p)$. V_e itself is probably a slowly varying function in most important regions of positron-space, but the difference between these two large quantities

$$\Delta(\vec{r}_p) = V_e(\vec{r}_p) - (\phi_p|V_e|\phi_p) \tag{3.25}$$

is itself small, and indeed vanishes upon integration with a weighting factor of $|\phi_p|^2$. Thus we may write Eq. (3.18) as

$$(F_p - \epsilon_p)\phi_p \quad , \tag{3.26}$$

where ϵ_p is the positronic binding energy and F_p is the positronic analog of the electronic Hartree-Fock operator to be derived in Sec. III. F_p is

$$F_p = h_p + 2\sum_i (\phi_i|g_{\mu p}|\phi_i) + \tau_p + \Delta_p \quad . \tag{3.27}$$

The first two terms above, the bare-nucleus Hamiltonian plus the electronic attraction terms, are just what one would expect to appear in a simple orbital theory. One might not have guessed the kinetic coupling term τ_p or the last term Δ_p, the physical significance of which is not as apparent. Both τ_p and Δ_p arise from electron-positron correlation, as can be seen by observing that they disappear if the electronic orbitals are made independent of $\vec{r}_p$. In any case, Δ_p does not contribute directly to the binding energy of the positron.

ϵ_p may also be written as the small difference between two large calculated quantities,

$$\epsilon_p = E - (\phi_p|V_e|\phi_p) \quad . \tag{3.28}$$

In actual computation one will obtain a numerical value for ϵ_p as the eigenvalue in Eq. (3.26), rather than by directly evaluating the right of Eq. (3.28). On the basis of extensive experience of many workers with purely electronic systems, we expect the value of ϵ_p determined in this way to be more accurate than either quantity on the right side of Eq. (3.28).

C. Electronic Equations

We now vary ϕ_i^* in the functional J [Eq. (3.17)]. The variation is straightforward if we remember that ϕ_i^* appears there not only explicitly but also implicitly in J_i, K_i, and $\vec{B}_i$, and that the variation takes place in two-body i, p space. The result is

$$[h_\mu + g_{\mu p} - \tfrac{1}{2}\nabla_p^2 + \sum_j (2J_j - K_j - \vec{B}_j \cdot \nabla_p)]\phi_i = \sum_j \lambda_{ij}\phi_j \quad , \tag{3.29}$$

where we have divided through by the positronic density $|\phi_p|^2$. Thus the ϕ_i are strictly not defined on the nodes of ϕ_p. Since these regions of ambiguity have lower dimensionality than the 6-space in which each ϕ_i is defined, we render ϕ_i continuous and differentiable everywhere simply by defining it to satisfy Eq. (3.29) when $|\phi_p|^2 = 0$.

That the off-diagonal Lagrange multipliers may be set equal to zero without loss of generality follows from the Hermiticity of the operator in brackets on the left-hand side. The proof is practically identical to the analogous proof for purely electronic systems given by Roothaan[7] so we do not repeat it here. The only differences are that here the effective electronic operator is more complicated, and the unitary transformation matrix $\underline{U}$ which diagonalizes $\underline{\lambda}$ has elements which are functions of $\vec{r}_p$.

We may therefore write

$$\begin{aligned} &(F_e - \epsilon_i)\phi_i = 0 \quad , \\ &F_e = h_\mu + g_{\mu p} - \tfrac{1}{2}\nabla_p^2 + \sum_j (2J_j - K_j - \vec{B}_j \circ \nabla_p) \quad , \end{aligned} \tag{3.30}$$

where we have made the substitution $\epsilon_i = \lambda_{ii}$.

This is a two-particle equation containing (first three terms) the Laplacians for the ith electron as well as the positron, and the terms for the Coulomb interactions between the electron-nucleus and electron-positron pairs. The positron-nucleus interaction term does not appear in the equation. The summand consists of the familiar electronic repulsion term in the Hartree-Fock approximation and the term for the indirect kinetic coupling of electron pairs, which we discussed in Sec. III B.

The eigenvalue ϵ_i depends upon $\vec{r}_p$. The situation is reminiscent of the Born-Oppenheimer approximation for purely electronic molecules in which the electronic eigenvalues depend upon the nuclear conformation. We emphasize that the similarity is coincidental, and that in our approach, only the nuclei are clamped.

The binding energy of the ith electron is

$$\langle\psi_p|\epsilon_i|\psi_p\rangle = (\phi_p|\epsilon_i|\phi_p) \quad . \tag{3.31}$$

IV. DISCUSSION

A. Solving the SCF Equations

Once the electronic equations [Eq. (3.30)] are solved, the positronic equation (3.26) is easy to solve, since the latter is "nearly" linear. If it were not for the term Δ_p, no iterations for self-consistency would be required. Since Δ_p is small, one might reasonably expect rapid convergence. Perturbation schemes suggest themselves and are discussed below.

In contrast, the electronic equations have large nonlinear terms. However, the positronic orbital ϕ_p does not appear in Eq. (3.30), whereas all the ϕ_i occur in Eq. (3.26). Therefore, one should first solve for the self-consistent set $\{\phi_i\}$ without reference to ϕ_p, and then calculate ϕ_p. There is no need to iterate between $\{\phi_i\}$ and ϕ_p.

In principle one can solve Eq. (3.30) by iteration among $\{\phi_i\}$ in spite of the functional dependence of the eigenvalue. However, in practice this approach is unattractive owing to the complexity of some of the terms in Eq. (3.30). Even for the simplest systems – an atom with a positron – the J_j term is formally the same as a three-center, one-electron nuclear attraction integral. $K_j\phi_i$ also gives rise to such an integral. Evaluation of these terms by transforming to ellipsoidal coordinates and integrating[8] leads to a function of $\vec{r}_\mu$ and $\vec{r}_p$ which is given as an infinite expansion in Legendre functions of the coordinates $(r_\mu \pm r_{\mu p})/r_p$.

On the other hand, the expansion method[7] appears to offer a practical alternative for atomic systems, for which the matrix elements of J_j and K_j are two-center electronic repulsion integrals of the exchange type, integrated over the "internuclear" distance. Let us expand the orbitals ϕ_p and ϕ_i as follows:

$$\phi_p(\vec{r}_p) = \sum_k \eta_k(\vec{r}_p) b_{kp} , \tag{4.1}$$

$$\phi_i(\vec{r}_\mu, \vec{r}_p) = \sum_m \chi_m(\vec{r}_\mu, \vec{r}_p) c_{mi} , \tag{4.2}$$

where $\{\eta_k(\vec{r}_p)\}$ and $\{\chi_m(\vec{r}_\mu, \vec{r}_p)\}$ are two linearly independent basis sets. The number of basis functions of each symmetry type in $\{\chi_m\}$ is taken large enough to provide the desired number of each type of electronic orbitals. We assume that the sets are normalized in the sense

$$\int d\vec{r}_p |\eta_k(\vec{r}_p)|^2 = (\eta_k|\eta_k) = 1 , \tag{4.3}$$
$$\int d\vec{r}_\mu |\chi_m(\vec{r}_\mu, \vec{r}_p)|^2 = (\chi_m|\chi_m) = 1 .$$

Regarding the sets $\{\eta_k\}$, $\{\chi_m\}$, $\{b_{kp}\}$, and $\{c_{mi}\}$ as column vectors,

$$\underline{\eta} = \begin{bmatrix} \eta_1 \\ \eta_2 \\ \cdot \\ \cdot \\ \cdot \\ \eta_k \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} , \quad \underline{\chi} = \begin{bmatrix} \chi_1 \\ \chi_2 \\ \cdot \\ \cdot \\ \cdot \\ \chi_m \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} , \tag{4.4}$$

$$\underline{b}_p = \begin{bmatrix} b_{ip} \\ b_{2p} \\ \cdot \\ \cdot \\ \cdot \\ b_{kp} \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} , \quad \text{and } \underline{c}_i = \begin{bmatrix} c_{1i} \\ c_{2i} \\ \cdot \\ \cdot \\ \cdot \\ c_{mi} \\ \cdot \\ \cdot \\ \cdot \end{bmatrix} , \tag{4.5}$$

we have (T means transpose and † means adjoint ≡ complex transpose)

$$\phi_p = \underline{\eta}^T \underline{b}_p , \tag{4.6}$$

$$\phi_i = \underline{\chi}^T \underline{c}_i . \tag{4.7}$$

We define the matrix elements of a positronic operator M^p_{op} as

$$[\underline{M}^p]_{kl} = M^p_{kl} = (\eta_k | M^p_{op} | \eta_l) . \tag{4.8}$$

Then

$$\begin{aligned}(\phi_p | M^p_{op} | \phi_p) &= \sum_k b^*_{kp} \sum_l b_{lp} (\eta_k | M^p_{op} | \eta_l) , \\ &= \underline{b}^\dagger_p \underline{M}^p b_p .\end{aligned} \tag{4.9}$$

Normalization is indicated as

$$(\phi_p | \phi_p) = \sum_k b^*_{kp} \sum_l b_{lp} (\eta_k | \eta_l) = \underline{b}^\dagger \underline{S}^p \underline{b} = 1 . \tag{4.10}$$

Forming the J functional [Eq. (3.17)] in terms of the variational parameters b_{kp} is a straightforward matter of substituting with Eq. (4.6).

Variation leads to

$$(\underline{H}^p - E\underline{S}^p) \underline{b}_p = 0 , \tag{4.11}$$

which is the matrix representation of Eq. (3.18). Here

$$\underline{H}^p = \underline{h}_p + \underline{X} + \underline{V}_e , \tag{4.12}$$

where:

$$\begin{aligned}[\underline{h}_p]_{kl} &= (\eta_k | h_p | \eta_l) , \\ [\underline{X}]_{kl} &= (\eta_k | 2\sum_i (\phi_i | g_{\mu p} - \tfrac{1}{2}\nabla^2_p - \tfrac{1}{2}\sum_j \vec{B}_j \cdot \nabla_p | \phi_i) | \eta_l) , \\ [\underline{V}_e]_{kl} &= (\eta_k | \sum_i (\phi_i | 2h_\mu + \sum_j (2J_j - K_j) | \phi_i) | \eta_l) .\end{aligned} \tag{4.13}$$

We define matrix elements of a one-electron operator M^i_{op} as

$$\begin{aligned}[\underline{M}^i]_{mn} &= (w | (\chi_m | M^i_{op} | \chi_n) |) \\ &= \int d\vec{r}_p w^*(\vec{r}_p) (\chi_m | M^i_{op} | \chi_n),\end{aligned} \tag{4.14}$$

where $w(\vec{r}_p)$ is a weighting factor which will be chosen later for convenience in performing integrations. Orthonormalization of the set $\{\phi_i\}$ is assured by requiring

$$(w|(\phi_i|\phi_j)|) = \sum_m c_{mi}^* \sum_n c_{nj} (w|(\chi_m|\chi_n)|) = \underline{c}_i^\dagger S^i \underline{c}_j = \delta_{ij} \,. \tag{4.15}$$

Application of familiar procedures yields the analog of Eq. (3.30):

$$\begin{aligned}(\underline{F}^i - \epsilon_i \underline{S}^i)\underline{c}_i = 0 \,,\\ [\underline{F}^i]_{mn} = (w|(\chi_m|h_\mu + g_{\mu p} - \tfrac{1}{2}\nabla_p^2\\ + \textstyle\sum_j (2J_j - K_j - \vec{B}_j \cdot \nabla_p)|\chi_n)|) \,.\end{aligned} \tag{4.16}$$

Examination of the matrix elements indicated in Eqs. (4.13) and (4.16) shows that for atom-plus-positron systems, all the integrals are familiar. For example, the electronic repulsion integrals $(\eta_k|(\phi_i|J_j|\phi_i)|\eta_l)$, $(\eta_k|(\phi_i|K_j|\phi_i)|\eta_l)$, $(w|(\chi_m|J_j|\chi_n)|)$, and $(w|(\chi_m|K_j|\chi_n)|)$ are, for $w = |\phi_p|^2$, linear combinations of

$$(\eta_k(\vec{r}_p)|(\chi_m(\vec{r}_\mu, \vec{r}_p)\chi_{m'}(\vec{r}_\nu, \vec{r}_p)|1/r_{\mu\nu}|\chi_n(\vec{r}_\mu, \vec{r}_p)\chi_{n'}(\vec{r}_\nu, \vec{r}_p))|\eta_l(\vec{r}_p)) \,. \tag{4.17}$$

One possible choice of basis set is to take each χ_i to be a product of a nuclear-centered Slater-type orbital, a positron-centered Slater s-type orbital, and a normalization factor $N_i(r_p)$. Then (4.17) is a two-center exchange integral which is integrated over the "internuclear distance" $\vec{r}_p$ with a weighting factor of $\eta_k^*(\vec{r}_p)\eta_l(\vec{r}_p) N_m^*(r_p) N_{m'}^*(r_p) N_n(r_p) N_{n'}(r_p)$. Similarly, the integrals involving the operator $\vec{B}_j \cdot \nabla_p$ are linear combinations of

$$\begin{aligned}(\eta_k|(\chi_m|\nabla_p|\chi_n)\cdot(\chi_{m'}|\nabla_p|\chi_{n'})|\eta_l) = \tfrac{1}{2}(\eta_k|(\chi_m\chi_{m'}|\nabla_p^2(\chi_n\chi_{n'}))\\ - (\chi_m|\chi_n)(\chi_{m'}|\nabla_p^2|\chi_{n'}) - (\chi_{m'}|\chi_{n'})(\chi_m|\nabla_p^2|\chi_n)|\eta_l) \,.\end{aligned} \tag{4.18}$$

B. Simplifications from Perturbation Theory

In solving Eq. (3.26), one might sensibly omit the correlation potential term Δ_p since it contributes only indirectly to ϵ_p and ϕ_p. One might also solve Eqs. (3.26) and (3.30) without the small three-body terms, and calculate a correction term to the orbitals with perturbation theory. That is, let us expand

$$\begin{aligned}F_e &= \tilde{F}_e + F_e' + \cdots \,,\\ F_p &= \tilde{F}_p + F_p' + \cdots \,,\\ \epsilon_i &= \tilde{\epsilon}_i + \epsilon_i' + \cdots \,,\\ \phi_i &= \tilde{\phi}_i + \phi_i' + \cdots \,,\end{aligned} \tag{4.19}$$

and so forth, where

$$\begin{aligned}F_e' &= -\textstyle\sum_j \tilde{\vec{B}}_j \cdot \nabla_p \,,\\ F_p' &= -\textstyle\sum_i \sum_j (\tilde{\phi}_i|\tilde{\vec{B}}_j \cdot \nabla_p|\tilde{\phi}_i) + \tilde{\delta}_p \,,\end{aligned} \tag{4.20}$$

and

$$\begin{aligned}\tilde{\vec{B}}_j &= -\nabla_p \tilde{\phi}_j (\tilde{\phi}_j| \,,\\ \tilde{\Delta}_p &= \tilde{V}_e(\vec{r}_p) - (\tilde{\phi}_p|\tilde{V}_e(\vec{r}_p)|\tilde{\phi}_p) \,,\end{aligned} \tag{4.21}$$

where the definition of $\tilde{V}_e(\vec{r}_p)$ involves obvious modifications of Eqs. (3.20), (3.3), and (3.4). Rather than solve Eqs. (3.26) and (3.30) directly, we might find it simpler to solve first the system

$$\begin{aligned}(\tilde{F}_e - \tilde{\epsilon}_i)\tilde{\phi}_i = 0 \,,\\ (\tilde{F}_p - \tilde{\epsilon}_p)\tilde{\phi}_p = 0 \,,\end{aligned} \tag{4.22}$$

and then calculate corrections by solving

$$\begin{aligned}(\tilde{F}_e - \tilde{\epsilon}_i)\phi_i' + (F_e' - \epsilon_i')\tilde{\phi}_i = 0 \quad ,\\ (\tilde{F}_p - \tilde{\epsilon}_p)\phi_p' + (F_p' - \epsilon_p')\tilde{\phi} = 0 \quad .\end{aligned} \tag{4.23}$$

Other perturbative approaches easily come to mind. For inner shells which are not very much influenced by the presence of a positron, a perturbation scheme would seem to offer a reasonable alternative to the solution of the full SCF equations (3.30) and (3.26), especially for large molecules for which semiempirical methods must be used in any case. Such an approach has been often suggested in the literature to deal with low-energy positron-atom scattering. We defer further discussion to a future communication.

V. PREVIOUS BOUND-STATE CALCULATIONS

In subsequent papers we will apply the equations derived here [Eqs. (3.26) and (3.30)] to various systems. We now conclude the present paper by relating our equations to previous work on one-positron, many-electron systems. Lebeda and Schrader[9] have recently reviewed calculations on bound systems with one or two electrons, and we here emphasize more complicated systems. Our main interest is in atoms and molecules, but we will comment on a portion of the work on solids and scattering systems as well.

If one assumes that the electrons see a fixed positron, and that the positron interacts with the time-averaged electrons, one arrives at the following equations:

$$[h_\mu + g_{\mu p} + \textstyle\sum_j (2J_j - K_j) - \epsilon_i]\,\phi_i = 0 \;, \tag{5.1a}$$

$$[h_p + 2\textstyle\sum_i (\phi_i | g_{\mu p} | \phi_i) + \tau_p + \Delta_p - \epsilon_p]\phi_p = 0 \;. \tag{5.1b}$$

These equations embody the "adiabatic approximation."[10] Equation (5.1a) is Eq. (3.30) with the terms $-\frac{1}{2}\nabla_p^2$ and $-\sum_j \vec{B}_j \cdot \nabla_p$ removed from the effective one-electron Hamiltonian. Equation (5.1b) is identical to Eq. (3.26). If the term τ_p is removed from Eq. (5.1b) we obtain the "Born-Oppenheimer approximation." In the "adiabatic approximation" the $\vec{r}_p$ dependence of ϕ_i is parametric in Eq. (5.1a) and functional in (5.1b); in the "Born-Oppenheimer approximation" the dependence is parametric in both equations. Here we use the terms "adiabatic approximation" and "Born-Oppenheimer approximation" to describe the treatment of the motion of the positron. In either case the nuclei are considered only as fixed point charges.

In the Hartree-Fock approximation one treats the motions of all the light particles on an equal footing, and averages all Coulomb interactions between them. The Hartree-Fock equations are

$$[h_i + (\phi_p | g_{\mu p} | \phi_p) + \textstyle\sum_j (2J_j - K_j) - \epsilon_i]\,\phi_i = 0 \,, \tag{5.2a}$$

$$[h_p + 2\textstyle\sum_i (\phi_i | g_{\mu p} | \phi_i) - \epsilon_p]\phi_p = 0 \;, \tag{5.2b}$$

which were first given by Chang Lee[3] and have been solved for PsH by Goldanskii, *et al.*[11] Equation (5.2a) may be obtained from (5.1a) by replacing $g_{\mu p}$ by its average, $(\phi_p | g_{\mu p} | \phi_p)$; then ϕ_i is independent of $\vec{r}_p$, and the terms τ_p and Δ_p in (5.1b) are identically zero, giving (5.2b).

In the earliest calculation on a many-electron system, PsCl, Simons[12] omitted the term $(\phi_p | g_{\mu p} | \phi_p)$ in Eq. (5.2a). We will refer to this approximation as the "unpolarized Hartree-Fock approximation." In this approximation the effect of the positron on the electrons is ignored completely. The advantage of this approach is that one desiring to do a calculation may often find the required electronic orbitals in the literature. Simons devised an approximate positronic orbital ϕ_p for PsCl and then calculated the error in the energy resulting from errors in ϕ_p, using first-order perturbation theory.

In calculations on metallic solids, many authors have used unpolarized Hartree-Fock orbitals for the core electrons and a constant for the electronic density from the valence electrons. In the first such calculation, DeBenedetti *et al.*,[13] used a constant also for the positron distribution. Otherwise, an equation of the form of (5.2b) results, which Donovan and March,[14] and Berko and Plaskett[15] solved using the cell model. This method, which is the solid-state equivalent of the unpolarized Hartree-Fock approximation employed by Simmons, has been applied to a variety of solid systems.[16] Brandt, Eder, and Lundqvist[17] use a related method for solid LiH. These authors add potential terms to the effective Hamiltonian to correct for interelectronic correlations and the Madelung energy.

In a calculation on solid argon, Woll and Rose[18] employ unpolarized Hartree-Fock atomic orbitals for the electrons and the adiabatic approximation for the positron. In addition, the Δ_p term is ignored and the τ_p term is approximated with first-order perturbation theory using the unpolarized Hartree-Fock electronic orbitals for the zeroth-order approximation. The resulting sums are evaluated by using the Unsold[19] approximation followed by closure. The resulting τ_p is

$$\tau_p = -(1/\Delta E)\textstyle\sum_i [(\phi_i | g_{\mu p}^2 | \phi_i) - \textstyle\sum_j |(\phi_i | g_{\mu p} | \phi_j)|^2] \,, \tag{5.3}$$

where ΔE is the excitation energy of the lowest excited state of the argon atom. Contributions from neighboring cells are ignored, and core electrons are accounted for simply by reducing the nuclear charge to that of the ion core. Sums in (5.1b) and (5.3) are thus taken over valence electrons only. The resulting equation for ϕ_p was solved using the cell model.

In a large number of calculations on positron-atom and -molecule complexes in which the atom or molecule is electrically neutral and the positron is unbound, various authors have adopted the unpolarized Hartree-Fock approximation for the electrons and have used for ϕ_p the asymptotic form $c\,e^{i\vec{k}\cdot\vec{r}_p}$, where c is a constant. Then the positronic charge density is a constant, Eq. (2.9) reduces to $\tau_{2\gamma}^{-1} = \pi\alpha^3 n|c|^2$, and Eq. (2.10) is simply the electronic momentum distribution of the neutral atom or molecule in the Hartree-Fock approximation. An adaptation of this approach was first applied to molecules by Columbino, *et al.*[20] Recently Hogg and co-workers[21] have generalized their approach by solving a simple modified form of Eq. (5.2b) for the positronic orbital.

Besides a constant for the positronic charge density, a variety of other functions have been used, including even the Δ function.[4]

None of the methods described so far in this section correctly treat the crucial short-range electron-positron correlation. It is easy to see that the electron-positron cusp value is −1 for the adiabatic and Born-Oppenheimer approximations, and zero for the Hartree-Fock and related approximations. Experience with other systems by ourselves,[9, 22] and by many other authors, suggests that the annihilation rate calculated in the adiabatic and Born-Oppenheimer approximations will be considerably too large, while that calculated in the Hartree-Fock and unpolarized Hartree-Fock approximations will be much too small. It should be noted here that the Hartree-Fock and unpolarized Hartree-Fock approaches require by far the least labor, and may yield reasonably accurate angular correlation curves.

The work of Dinh Van Hoang[23] on e^+-alkali atoms is not easily described in terms of the foregoing equations in this section. His calculation on e^+Li is typical. He writes for the wave function of the system,

$$\Psi = \phi_{\text{core}}(\vec{r}_1, \vec{r}_2)\phi_{\text{val}}(\vec{r}_3, \vec{r}_p) , \tag{5.4}$$

where ϕ_{core} is the simple screened hydrogenic function,

$$\phi_{\text{core}} = Ne^{-(z-\frac{5}{16})(r_1+r_2)} \tag{5.5}$$

and ϕ_{val} is

$$\phi_{\text{val}} = N' r_p^2 e^{-\beta(r_3+r_{3p})} . \tag{5.6}$$

z is the nuclear charge, N and N' are normalizing factors, and β is a variational parameter. We do not discuss his results but simply point out that, in this approach, spin is incorrectly treated, the wave function is not anti-symmetric under electron intercharge, the orbital for the valence electron is strongly nonorthogonal to that of the core electrons, and no choice of the parameter β will simultaneously satisfy the cusp conditions between attractive pairs of particles. Somewhat similar comments apply to calculations by Majumdar and coworkers.[24]

Schmelev[25] uses the term "Born-Oppenheimer approximation" to describe his calculation on the system e^+H. However, it appears to us that Schmelev's method is much like our own, embodied in Eqs. (3.26) and (3.30).

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