

Modified Perturbation Theory for Atoms and Molecules Based on a Hartree-Fock ϕ_0^*

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The improvement of Hartree-Fock wavefunctions by perturbation theory is hampered by slow convergence with the usual choice of

$$H_0 = \sum_{i=1}^N F(i),$$

where F denotes the one-electron Hartree-Fock Hamiltonian. The slow convergence is usually attributed to the unphysical nature of the excited states of F , which do not describe electrons moving in the field of the nuclei, shielded by $N-1$ electrons. It is shown how to redefine F so that the zeroth-order wavefunction still remains the Hartree-Fock wavefunction but so that the excited states of F correspond to an electron moving in the field of the nuclei screened by $N-1$ electrons. The redefined F thus results in a more appropriate H_0 . Calculations of some second-order polarization and semi-internal correlation energies in first-row atoms are given to illustrate the use of the redefined F .

I. INTRODUCTION

The electronic wavefunction ψ for an atom or molecule may be partitioned into a restricted Hartree-Fock (RHF) wavefunction¹⁻³ ϕ_{RHF} and a correlation wavefunction χ ,

$$\psi = \phi_{\text{RHF}} + \chi, \quad (1)$$

with the normalization convention

$$\langle \phi_{\text{RHF}} | \phi_{\text{RHF}} \rangle = 1, \quad (2)$$

$$\langle \phi_{\text{RHF}} | \chi \rangle = 0. \quad (3)$$

This paper is concerned with the computation of χ by perturbation theory.

Perturbation theory, starting from a RHF ϕ_0 (by ϕ_0 we mean the zeroth-order function in perturbation theory), has been discussed from different viewpoints by Sinanoğlu⁴ and by Goldstone⁵ for closed-shell states and by Kelly⁶ and Silverstone and Sinanoğlu⁷ for open-shell states. A common feature of these discussions concerned the choice of an unperturbed Hamiltonian H_0 equal to the "Hartree-Fock Hamiltonian,"

$$H_0 = H_{\text{RHF}}, \quad (4)$$

$$H_{\text{RHF}} = \sum_{i=1}^N F(i). \quad (5)$$

Here N is the number of electrons, and F denotes the RHF one-electron Hamiltonian, defined, e.g., by Eq. (36) of Ref. 2. In calculations on beryllium, however, Kelly⁸ found slow convergence for the perturbation theory. He argued^{8,9} that since the "virtual orbitals" of F

almost all lay in the continuum, the eigenvalue spectrum of H_{RHF} was extremely dissimilar to the spectrum of H , and poor convergence was the consequence. Kelly found that removing the Coulomb and exchange operators of one orbital in F gave F bound excited states, made the resulting H_0 more like H , and greatly improved convergence.^{6,9} However, his ϕ_0 was no longer ϕ_{RHF} .

Epstein,¹⁰ in discussing "What is H_0 ?" pointed out that despite the automatic production, from the calculation of ϕ_{RHF} , of H_{RHF} with the property

$$H_{\text{RHF}}\phi_{\text{RHF}} = E_0\phi_{\text{RHF}}, \quad (6)$$

H_{RHF} is not necessarily a good choice for H_0 . In looking for a better H_0 , he showed¹⁰ by example that no F existed with a local potential in the Hartree-Fock case, although a rather complicated local, but many-electron H_0 could be obtained for ϕ_{RHF} .^{11a} Epstein earlier had suggested using a separable (but otherwise unspecified) nonlocal potential in F .^{11b}

Our purpose here is to give a simple, intuitive, mathematically rigorous redefinition of F which retains $\phi_0 = \phi_{\text{RHF}}$ (unlike Kelly), which makes H_0 more like H (like Kelly), and which provides a partial but concrete answer to Epstein's question.¹² Some calculations on first-row atoms, based on the redefined F , are given to illustrate the use of the redefined F .

II. WHAT IS F ?

In this section we discuss the choice of F from the point of view of calculating χ by perturbation theory. For simplicity, consider an atom or molecule with only one open shell. Assume that the (occupied) RHF spin orbitals $\{\phi_i | i=1, 2, \dots, M\}$ have already been

¹⁰ S. T. Epstein, in *Perturbation Theory and Its Application to Quantum Mechanics*, C. H. Wilcox, Ed. (John Wiley & Sons, Inc., New York, 1966).

^{11a} S. T. Epstein and J. H. Karl, *J. Chem. Phys.* **44**, 4347 (1966).

^{11b} S. T. Epstein, *J. Chem. Phys.* **41**, 1045 (1964).

¹² Very specific F 's were constructed by S. T. Manson [*Phys. Rev.* **145**, 35 (1966)] when calculating autoionization rates in He and Li. Manson's F 's have a few of the properties of the more general F 's constructed here. The authors are indebted to Professor Saul T. Epstein for pointing out Manson's paper.

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¹ C. C. J. Roothaan, *Rev. Mod. Phys.* **23**, 69 (1951).

² C. C. J. Roothaan, *Rev. Mod. Phys.* **32**, 179 (1960).

³ F. W. Birss and S. Fraga, *J. Chem. Phys.* **38**, 2552 (1963).

⁴ O. Sinanoğlu, *Proc. Roy. Soc. (London)* **A260**, 379 (1961).

⁵ J. Goldstone, *Proc. Roy. Soc. (London)* **A239**, 267 (1957).

⁶ H. P. Kelly, *Phys. Rev.* **144**, 39 (1966).

⁷ H. J. Silverstone and O. Sinanoğlu, *J. Chem. Phys.* **44**, 1899 (1966).

⁸ H. P. Kelly, *Phys. Rev.* **131**, 684 (1963).

⁹ H. P. Kelly, *Phys. Rev.* **136**, B896 (1964).

determined. These spin orbitals are eigenfunctions of Roothaan's Hamiltonian [Eq. (36) of Ref. 2], which we now denote by F_R ,

$$F_R \phi_i = \epsilon_i \phi_i. \quad (7)$$

The set of M spin orbitals we call the RHF sea, which includes, in addition to the spin orbitals appearing in the N electron ϕ_{RHF} , those spin orbitals required to make closed shells.

The major problem in choosing F is what F should be for excited states. To bring out this point, let P_i denote a projection operator for state ϕ_i in the RHF sea,

$$P_i = |\phi_i\rangle\langle\phi_i|, \quad i=1, \dots, M. \quad (8)$$

Also, let

$$P = \sum_{i=1}^M P_i, \quad (9)$$

$$Q = 1 - P. \quad (10)$$

Both F (which will be the redefined Hamiltonian) and F_R (Roothaan's Hamiltonian) do not connect "P space" with "Q space":

$$F = PFP + QFQ, \quad (11)$$

$$F_R = PF_R P + QF_R Q. \quad (12)$$

From Eqs. (7) and (8), we have

$$PF_R P = \sum_{i=1}^M \epsilon_i P_i. \quad (13)$$

Moreover, we can write, generally,

$$PFP = \sum_{i=1}^M \epsilon_i P_i. \quad (14)$$

(We use ϵ_i and δ_i for the eigenvalues of F_R and F , respectively.) Thus, to specify F is to specify the δ_i , ($i=1, 2, \dots, M$) and QFQ .

Three general requirements for F are:

(1) Physical: Excited (i.e., virtual) eigenfunctions of F (i.e., of QFQ) should resemble an electron moving in the field of the nuclei screened by $N-1$ electrons.¹³

(2) Physical: The orbital energies should bear some relation to ionization potentials, à la Koopmans' theorem.¹⁴

(3) Mathematical convenience: F should be Hermitian and commute with all relevant symmetry operators, such as \mathbf{l} and \mathbf{s} for atoms.

Requirements (1) and (2) are to make H_0 something like H . Roothaan's F_R satisfies requirement (3) but not (1) and (2).

The above considerations do not determine a unique F . Neither are there any uniquely important criteria which would lead to a unique F . In the next section we give a recipe for a particular F satisfying the three

general requirements, but here we first make an observation on the form of F . Let h_{BN} denote the Hamiltonian for an electron moving in the field of the bare nuclei (BN). It would be convenient for F to have the standard form

$$F = h_{\text{BN}} + V, \quad (15)$$

where the potential V does not explicitly involve h_{BN} . Roothaan's F_R has this form,²

$$F_R = h_{\text{BN}} + V_R. \quad (16)$$

Suppose that F had been specified through the M δ_i and a potential $U(r)$ via

$$F = \sum_{i=1}^M \delta_i P_i + Q(h_{\text{BN}} + U)Q. \quad (17)$$

Then from Eqs. (11)-(17), F can be cast in standard form (15) if V is given by

$$V = QU(r)Q + V_R - QV_R Q + \sum_{i=1}^M (\delta_i - \epsilon_i) P_i. \quad (18)$$

III. RECIPE FOR F

An intuitive formulation of $U(r)$ and the δ_i is easily obtained. Consider first Requirement (2) above. The δ_i cannot of course correspond exactly to ionization potentials, because ionization potentials depend on the total spin and other total quantum numbers (e.g., L for atoms) of the nonionized and ionized state of the atom or molecule.² One *can* however choose δ_i to represent an *average* ionization potential for an electron in a given shell, by averaging the ionization potential expressions computed from simple-orbital-type wavefunctions over the symmetry quantum numbers of the ionized state. Such a choice is easier to illustrate [see Eq. (33)] than to formulate precisely.

Next consider Requirement (1). Let J_μ^T and K_μ^T denote total Coulomb and exchange operators for the μ th shell, i.e., in spin-orbital notation,

$$J_\mu^T = \sum_{i(\phi_i \text{ in shell } \mu)} J_i, \quad (19)$$

$$K_\mu^T = \sum_{i(\phi_i \text{ in shell } \mu)} K_i. \quad (20)$$

Here J_i and K_i have their usual meanings as Coulomb and exchange operators for spin orbital ϕ_i . Let n_μ be the total number of spin orbitals in shell μ and $n_{\mu f_\mu}$ the actual number occupied in ϕ_{RHF} . A simple U , built only from J and K operators, satisfying Requirement (1), is

$$U(r) = \sum_{\mu \text{ (shells } \mu \text{ in } \phi_{\text{RHF}})} f_\mu (J_\mu^T - K_\mu^T) - (1/n_\nu) (J_\nu^T - K_\nu^T), \quad (21)$$

where ν is a shell, chosen for physical reasons, from which an electron has been "removed." This U [Eq. (21)] automatically satisfies Requirement (3) because of the appearance of total J^T and K^T operators for each shell. Equation (21) is illustrated by Eq. (32) below.

¹³ Compare Ref. 9.

¹⁴ T. Koopmans, *Physica* **1**, 104 (1933).

More complicated U 's could easily be defined by varying the coefficients in front of J_{μ}^T , K_{μ}^T , J_s^T , and K_s^T [cf. Kelly^{6,9}] to represent more accurately the average electron-electron repulsions, and by removing different orbitals for different symmetry virtual orbitals. For example, let Q_e and Q_o denote projection operators for even- and odd- l orbitals; a possible U for the ground configuration of oxygen (again, cf. Kelly⁶) is

$$U = J_{1s}^T - K_{1s}^T + J_{2s}^T - K_{2s}^T + \frac{2}{3}(J_{2p}^T - K_{2p}^T) - \frac{1}{2}Q_e(J_{2s}^T - K_{2s}^T)Q_e - \frac{1}{6}Q_o(J_{2p}^T - K_{2p}^T)Q_o. \quad (22)$$

Since the ϵ_i and $U(r)$ proposed above are physically motivated but mathematically arbitrary, their usefulness and usability must be demonstrated by numerical examples. Kelly's Be and O computations^{6,9} already exemplify the physics involved in the choice of H_0 , but differ in the choice of ϕ_0 . In the next section a few illustrative computations are presented to demonstrate how this choice of H_0 works.

IV. EXAMPLES

For examples we calculate some polarization and semi-internal correlation energies⁷ to second order. Polarization effects occur in open-shell states because the actual average electronic field an electron experiences from the other electrons does not have the full spin and spatial symmetry of the atom or molecule. The semi-internal correlations arise from terms in the wavefunction in which one electron makes a transition within the RHF sea into a not-completely-occupied spin-orbital while a second electron goes out of the sea. In first-row atoms the most important of these are described in configuration-interaction (CI) language by excitations of the type

$$1s^2 2s^2 2p^n \rightarrow 1s^2 2s 2p^n d. \quad (23)$$

(Other excitations, e.g., $1s^2 2s^2 2p^n \rightarrow 1s^2 2s^2 2p^{n-1} 4f$, which are also of a similar nature, are not discussed here.) The semi-internal correlation effect is intermediate in nature between nondynamical and dynamical correlations.

That such terms as Eq. (23) contribute significantly to $2s-2p$ correlation energies (-0.4 eV in B, -0.76 eV in Ne⁶⁺) was first noted by McKoy and Sinanoğlu.¹⁶ The sizable contribution to energy of effects represented by Eq. (23) can be inferred also from the work of Weiss,¹⁶ of Kelly,⁶ and of Schaeffer and Harris¹⁷ to be -0.83 eV in 3P carbon, -1.03 eV in 3P oxygen, and -0.52 eV in 2P boron, i.e., roughly 15%–20% of the total correlation energies.¹⁸ These authors, however, did not single out the particular effect as a physically distinct correlation effect. Their nature and physical origin became clear in the perturbation version of "nonclosed-shell many-electron theory."¹⁷ Detailed cal-

culations (not tied to perturbation theory) of specifically the internal and semi-internal correlations for first-row atoms have been carried out by Sinanoğlu, Öksüz, and Skutnik.¹⁹ A comparison of their nonperturbation results with the perturbation theory results of this paper would be interesting in assessing the rate of convergence of the present perturbation theory at least for these specific effects. Although these polarization and semi-internal correlation effects are interesting in themselves, they are calculated here because they form a convenient illustration of the considerations of Sec. II and III.

First consider the 2P ground state of boron,

$$\phi_{\text{RHF}} = \alpha 1s^2 2s^2 2p_{+\alpha}. \quad (24)$$

The corresponding Roothaan potential is

$$V_{\text{R}} = J_{1s}^T - K_{1s}^T + J_{2s}^T - K_{2s}^T - \frac{1}{3}Q(J_{2p}^T - K_{2p}^T) + \frac{1}{3}\{J_{2p}^T - K_{2p}^T, P^C + \frac{1}{3}P^O\}, \quad (25)$$

where

$$P^C = P_{1s\alpha} + P_{1s\beta} + P_{2s\alpha} + P_{2s\beta}, \quad (26)$$

$$P^O = P_{2p_{+\alpha}} + P_{2p_{0\alpha}} + P_{2p_{-\alpha}} + P_{2p_{+\beta}} + P_{2p_{0\beta}} + P_{2p_{-\beta}}, \quad (27)$$

and where $\{x, y\}$ denotes the anticommutator,

$$\{x, y\} = xy + yx. \quad (28)$$

If one were to use V_{R} [Eq. (25)] for calculating excitations represented by (23) by perturbation theory, certain difficulties would arise. The origin of these difficulties is that (i) an electron in a d orbital (which does not see the $\{ \}$ term in V_{R}) appears to be moving in the field of the nucleus, shielded by $4 - (1/5) = 19/5$ electrons, and (ii) the $2s$ eigenvalue of F_{R} is (artificially) too high. The ϵ_{2s} corresponding to F_{R} is^{20,21} (1 a.u. ~ 27.2 eV)

$$\epsilon_{2s} = -0.0245 \text{ a.u.}, \quad (29)$$

which is higher than the energy of the $3d$ orbital,²²

$$\epsilon_{3d} = -0.0808 \text{ a.u.}, \quad (30)$$

and which is an order of magnitude different from an experimental ϵ_{2s} ,²³

$$\epsilon_{2s}(\text{exptl}) = -0.519 \text{ a.u.} \quad (31)$$

¹⁹ O. Sinanoğlu, I. Öksüz, and B. Skutnik (unpublished); (cf. also B. Skutnik, Ph.D. thesis, Chemistry Department, Yale University, 1967).

²⁰ The Hartree-Fock orbitals were obtained from the work of E. Clementi, J. Chem. Phys. **38**, 996 (1963), and Document No. 7441, ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C.

²¹ Here the ϵ represents the eigenvalue of F_{R} [Eq. (38) of Ref. 2]. That these ϵ are *not* even approximately equal to ionization potentials was first pointed out by Roothaan (Ref. 2).

²² The ϵ_{3d} was estimated by minimizing the expectation value of F_{R} with a single Slater-type $3d$ orbital. Note the existence of bound excited states of F_{R} . In Kelly's examples, the F was defined differently from F_{R} , especially with regard to the Coulomb and exchange operators of the open shell. In any event, the H_0 based on F_{R} is still extremely dissimilar to H .

²³ The value of ϵ_{2s} (exptl) was estimated from the data given by C. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467 (1949), by subtracting the average energy of the $1s^2 2s 2p$ configuration of B II from the average energy of B I $1s^2 2s^2 2p$.

¹⁶ V. McKoy and O. Sinanoğlu, J. Chem. Phys. **41**, 2689 (1964).

¹⁷ A. W. Weiss, Phys. Rev. **162**, 71 (1967).

¹⁸ H. F. Schaeffer III and F. E. Harris, Phys. Rev. **167**, 67 (1968).

¹⁹ E. Clementi, J. Chem. Phys. **38**, 2248 (1963).

TABLE I. Second-order correlation energies of the type $\bar{\epsilon}_s^{P(2)}$ and $\bar{\epsilon}_{kl;m}^{(2)}$ for first-row atoms.^a

<i>k</i> or <i>kl</i> ; <i>m</i> ^b	Correlation energies (a.u.) ^c × 1000					Proportionalities resulting from symmetry
	B(² P)	C(³ P)	N(⁴ S)	O(³ P)	F(² P)	
2s	-0.54	-0.53		-0.34	-0.33	1
2s, 2p ₊ ; 2p ₀	-1.62					3
2s, 2p ₊ ; 2p ₋	-3.24	-3.16				6
2s, 2p ₀ ; 2p ₋		-1.58				3
2s, 2p ₊ β; 2p ₀ β				-1.01		3
2s, 2p ₊ β, 2p ₋ β				-2.02	-2.00	6
2s, 2p ₀ β; 2p ₋ β					-1.00	3
2sβ	-0.35	-0.35		-0.50	-0.48	1
2sβ, 2p ₊ ; 2p ₀	-1.04					3
2sβ, 2p ₊ ; 2p ₋	-2.07	-2.09				6
2sβ, 2p ₀ ; 2p ₋		-1.04				3
2sβ, 2p ₊ β; 2p ₀ β				-1.49		3
2sβ, 2p ₊ β; 2p ₋ β				-2.97	-2.90	6
2sβ, 2p ₀ β; 2p ₋ β					-1.45	3
2sβ, 2p ₊ ; 2p ₊ β	-1.74	-1.72	-1.70			1
2sβ, 2p ₊ ; 2p ₀ β	-5.21	-5.16	-5.09	-4.92		3
2sβ, 2p ₊ ; 2p ₋ β	-10.43	-10.31	-10.18	-9.83	-9.65	6
2sβ, 2p ₀ ; 2p ₊ β		-5.16	-5.09			3
2sβ, 2p ₀ ; 2p ₀ β		-6.87	-6.79	-6.56		4
2sβ, 2p ₀ ; 2p ₋ β		-5.16	-5.09	-4.92	-4.83	3
2sβ, 2p ₋ ; 2p ₊ β			-10.18			6
2sβ, 2p ₋ ; 2p ₀ β			-5.09	-4.92		3
2sβ, 2p ₋ ; 2p ₋ β			-1.70	-1.64	-1.61	1
Σ $\bar{\epsilon}^{(2)}$	-26.23 (-0.71 eV)	-43.11 (-1.17 eV)	-50.92 (-1.39 eV)	-41.09 (-1.12 eV)	-24.27 (-0.66 eV)	
$E(2s) (d) [^3D]^d$	5/2	25/6	5	25/6	5/2	
$\bar{\epsilon}_{2s\beta, 2p_+; 2p_-\beta}$						
$E(2s) (d) [^3D]$	-26.07 (-0.71 eV)	-42.96 (-1.17 eV)	-50.92 (-1.39 eV)	-40.96 (-1.11 eV)	-24.13 (-0.66 eV)	
E_{corr}^e	-125 (-3.40 eV)	-158 (-4.30 eV)	-188 (-5.12 eV)	-258 (-7.02 eV)	-324 (-8.82 eV)	

^a The orbital exponents for the 3d Slater-type basis functions are given in Table II.

^b For brevity, α spin functions are omitted. For instance, 2s denotes 2s α .

^c 1 a.u. = 27.21 eV. Energies were rounded after computation. Estimated accuracy is two significant figures.

^d The lion's share of Σ $\bar{\epsilon}^{(2)}$ is contributed by the "configuration"

1s³[(2s) (d) : ³D]2p³. The contribution is a simple multiple of

$$\bar{\epsilon}^{(2)}_{2s\beta, 2p_+; 2p_-\beta}$$

^e Total correlation energy as estimated by E. Clementi, Ref. 18, has been included for comparison.

On the other hand, the potential for the modified *F*, given by Eqs. (17) and (20) with $\nu=2s$, is

$$U(r) = J_{1s}^T - K_{1s}^T + \frac{1}{2}(J_{2s}^T - K_{2s}^T) + \frac{1}{8}(J_{2p}^T - K_{2p}^T),$$

(32)

and the appropriate ϵ_{2s} [see discussion between Eqs.

(17) and (18)] is^{22,24}

$$\epsilon_{2s} = \langle 2s | h_{\text{BN}} + U(r) + \frac{1}{2}(J_{2s}^T - K_{2s}^T) | 2s \rangle, \quad (33)$$

$$= -0.495 \text{ a.u.} \quad (34)$$

²⁴ The ϵ_{2s} defined by Eq. (33) is precisely the same as the eigenvalue η_{2s} of F_C [Eq. (32) of Ref. 2]. The numerical value (-0.49468 a.u.) was given by Clementi, Ref. 20.

TABLE II. Orbital exponents for 3d Slater-type basis functions.^a

Intermediate coupling of (2s) (<i>d</i>)	Orbital exponent				
	B	C	N	O	F
³ D	1.384	1.756	2.131	2.475	2.838
¹ D	0.975	1.250		1.650	1.950

^a A 3d basis function has the form $Y_2^m(\theta, \phi)r^2 \exp(-\zeta r)$, where Y_2^m denotes a spherical harmonic of order 2 and ζ is the "orbital exponent." The ³D ζ was chosen to optimize $\tilde{\epsilon}^{(2)}_{2s\beta, 2p+, 2p-, \beta}$, the ¹D ζ to optimize $\tilde{\epsilon}^{P(2)}_{2s} + \tilde{\epsilon}^{P(2)}_{2s\beta}$.

This ϵ_{2s} is close to the "experimental" value and is lower than the 3d-orbital energy²⁵ for F [Eqs. (17) and (32)],

$$\epsilon_{3d} = -0.0530 \text{ a.u.} \quad (35)$$

With the modified F defined above, we must now solve the first-order equations [Eqs. (37) and (38) of Ref. 7] for the polarization and semi-internal correlation functions, $f_k^{(1)}$ and $\hat{f}_{klm}^{(1)}$, and the corresponding second-order correlation energies. The effects represented by Eq. (23) correspond here to $k=2s\alpha$, $2s\beta$; $l=2p_+\alpha$; and $m=2p_0\alpha$, $2p_-\alpha$, $2p_+\beta$, $2p_0\beta$, $2p_-\beta$. The calculation can be carried out variationally²⁶ by minimizing [note that all the \hat{f} 's in Eqs. (36) and (37) have d symmetry]

$$\begin{aligned} \tilde{\epsilon}_k^{P(2)} = & 2 \langle \phi_k | J_{2p+\alpha} - K_{2p+\alpha} | \hat{f}_k^{(1)} \rangle \\ & + \langle \hat{f}_k^{(1)} | F - \epsilon_{2s} | \hat{f}_k^{(1)} \rangle, \quad (36) \end{aligned}$$

$$\begin{aligned} \tilde{\epsilon}_{klm}^{(2)} = & 2 \langle \phi_k \phi_l - \phi_l \phi_k | 1/r_{12} | \phi_m \hat{f}_{klm}^{(1)} \rangle \\ & + \langle \hat{f}_{klm}^{(1)} | F - \epsilon_{2s} | \hat{f}_{klm}^{(1)} \rangle. \quad (37) \end{aligned}$$

There is no difficulty from the Q in Eq. (17) because d orbitals are automatically orthogonal to s orbitals and p orbitals. The results are in Table I. We note here that the total d -symmetry $2s$ polarization and $(2s)(2p)$ semi-internal correlation energy in second order is -0.0263 a.u. (-0.716 eV). [For perspective, the expectation value of the correlation energy with (the part of) the first-order wavefunction calculated here is -0.0204 a.u. (-0.555 eV), and the best variational expectation value (with two 3d-type Slater-type orbitals, one for $2s3d$ ¹D, the other for ³D intermediate coupling) we obtained is -0.0215 a.u. (-0.585 eV). Sinanoğlu, Öksüz, and Skutnik²⁷ report -0.613 eV for semi-internal correlations in boron, but this value

²⁵ The ϵ_{3d} was estimated with an optimized 3d Slater-type orbital.

²⁶ The separated first-order equations in Ref. 7 are being "solved" here by applying the variation-perturbation method to each such equation. The calculations of Sinanoğlu, Öksüz, and Skutnik,²⁷ on the other hand, use the full variation method and CI to get the internal and semi-internal correlations.

²⁷ O. Sinanoğlu, I. Öksüz, and B. Skutnik (private communication); to appear in Ref. 19.

includes other additional semi-internal correlations than the type specified by Eq. (23).]

Similarly, the second-order polarization and semi-internal correlation energies of type $2s2p_i \rightarrow 2p_i d$ only [Eq. (23)] for the ground states of C, N, O, and F were calculated by the variation-perturbation approach. The U in each case corresponded to Eq. (32) with f_{2p} multiplying $(J_{2p}^T - K_{2p}^T)$. The ϵ_{2s} was given by Eq. (33) with the appropriate U . The results are given in Table I, the details of the bases in Table II.

Several observations can be made from Table I. First, note that there are certain relationships among the second-order energies resulting from symmetry. Next note that a given type of semi-internal energy $\tilde{\epsilon}_{klm}^{(2)}$ is fairly constant, decreasing slightly as one moves from B to F. [Only $\tilde{\epsilon}_{2s\beta, 2p+, 2p-, \beta}^{(2)}$ actually occurs in the highest L_z, S_z member of all B to F ground states. See Table I.] The $\tilde{\epsilon}_{2s\alpha}^{P(2)}$ for B and C are comparable with the $\tilde{\epsilon}_{2s\beta}^{(2)}$ for F and O, and vice versa. The main contribution to the correlation energy comes from the ³D modification of the 2s shell, i.e., the intermediate coupling $(2s)^2 \rightarrow (2s)(d)$ [³D], and is numerically equal to $\epsilon_{2s\beta, 2p+, 2p-, \beta}^*$ multiplied by 5/2, 25/6, 5, 25/6, and 5/2 for B, C, N, O, and F, respectively. The remaining contribution [$(2s)(d)$ ¹D] is less than 2% of the ³D value in each case, and in N it is rigorously zero. Because of the smallness of the $(2s)(d)$ ¹D contribution and the near constancy of $\tilde{\epsilon}_{2s\beta, 2p+, 2p-, \beta}^{(2)}$, the total d -type polarization and $(2s)(2p_i)$; $(2p_i)$ semi-internal correlation energies of the first-row atoms are approximately in the ratio 3:5:6:5:3. It is especially apparent that these total energies are not proportional to the number of $2p$ electrons. It is expected that the above conclusions have general validity even though the second-order energies are probably a 20%–30% overestimate of the exact energies.

These calculations are easy to carry out and illustrate the usefulness of a physically doctored perturbation theory.

V. SUMMARY

A simple reformulation of the one-electron Hartree-Fock Hamiltonian suitable for calculating correlation effects by perturbation theory has been given. The virtual states are eigenfunctions of $Q[h_{BN} + U(r)]Q$, where h_{BN} is the one-electron "bare nuclei" Hamiltonian, $U(r)$ a physically chosen potential representing the screening effects of the electrons, and Q is a projection operator. Various recipes are indicated for $U(r)$. Computations of symmetry and spin polarizations and semi-internal correlation energies in first-row atoms are given as examples.

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