

butions are of opposite sign, a measured value for the latter with an improved accuracy of 0.5% is obtained.

With regard to other calculations in these states, two independent values^{14,15} have been obtained for the 2^1P_1 isotope shift in agreement with the above theory^{2,3} to within 0.001 cm^{-1} ; none of these calculations could be distinguished in the present experiment. An earlier calculation of the 2^1S_0 isotope shift¹⁶ disagreed considerably with the above theory and with the present experiment.

A brief remark might be made regarding the isotope shift in the higher ($2^1S_0-n^1P_1$) lines. The isotope shift for the $5016\text{-}\text{\AA}$ ($2^1S_0-3^1P_1$) and $3964\text{-}\text{\AA}$ ($2^1S_0-4^1P_1$) transitions has been measured spectroscopically, and these values for $\nu(\text{He}^3)-\nu(\text{He}^4)$ may be compared with the above theory, where the calculation is identical to that for the ($2^1S_0-2^1P_1$) line (see Table I). The agreement is very good but the shifts are primarily due to the reduced-mass effect. With the reduced-mass contributions excluded,

TABLE I.

	Spectroscopy ^a	Spectroscopy ^b	Theory ^c
($2^1S_0-3^1P_1$)	-0.833 ± 0.005	-0.849 ± 0.003	-0.8443 cm^{-1}
($2^1S_0-4^1P_1$)	-1.150 ± 0.005	-1.165 ± 0.005	-1.1630 cm^{-1}

^aSee Ref. 4.^bSee Ref. 5.^cSee Refs. 2 and 3.

the theoretical shifts would be

$$(2^1S_0-3^1P_1): \nu_{\text{mp}}(\text{He}^3)-\nu_{\text{mp}}(\text{He}^4) = 0.0497 \text{ cm}^{-1};$$

$$(2^1S_0-4^1P_1): \nu_{\text{mp}}(\text{He}^3)-\nu_{\text{mp}}(\text{He}^4) = 0.0320 \text{ cm}^{-1}.$$

Hence, of the ($2^1S_0-n^1P_1$) series, the ($2^1S_0-2^1P_1$) line is clearly the most sensitive to the mass-polarization term.

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Hartree-Fock Theory with Exchange Cutoff*†

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A new Fock-type operator is defined which varies between the Hartree and the Hartree-Fock operator depending on a cutoff parameter in the exchange potential. The corresponding pseudo-Hartree-Fock equations require each orbital ϕ_i to behave asymptotically as $\exp[-(-2\epsilon_i)^{1/2}r]$. Calculations are reported for the Ne atom.

I. INTRODUCTION

Handy, Marron, and Silverstone¹ (hereafter HMS) have shown that the long-range behavior of Hartree-

Fock orbitals for atoms is

$$\phi_i \rightarrow \exp[-(-2\epsilon_{\text{smallest}})^{1/2}r] \text{ as } r \rightarrow \infty, \quad (1)$$

except for the case of an atom consisting entirely

of s electrons, for which the behavior is

$$\phi_i \rightarrow \exp[-(-2\epsilon_i)^{1/2}r] \text{ as } r \rightarrow \infty. \quad (2)$$

A particular consequence of Eqs. (1) and (2) is that Be ($1s^2 2s^2$) has orbitals which die away with each orbital having its own tail, whereas B ($1s^2 2s^2 2p$) has orbitals all of which die away in the same manner. We feel that this behavior is an artifact of the Hartree-Fock model.

In this paper an alternative Hartree-Fock procedure is proposed. The model to be developed forces the Hartree-Fock orbitals to have the behavior of Eq. (2) in all cases.

II. THE HARTREE-FOCK LONG-RANGE PROBLEM

In the standard Hartree-Fock theory for closed-shell atoms, one solves the equation

$$F\phi_j = \epsilon_j\phi_j, \quad j = 1, \dots, N \quad (3)$$

where F in canonical form is given by

$$F = -\frac{1}{2}\nabla^2 - Z/r + \sum_i (2J_i - K_i), \quad (4)$$

with

$$J_i f(1) = f(1) \int \phi_i^*(2) \phi_i(2) (1/r_{12}) dv(2), \quad (5a)$$

$$K_i f(1) = \phi_i(1) \int \phi_i^*(2) f(2) (1/r_{12}) dv(2). \quad (5b)$$

In general, the operator F of Eq. (4) is the same operator for each orbital, which automatically produces orthogonality between different orbitals.

If the self-exchange terms are removed from the operator F , then each orbital becomes an eigenfunction of a different operator and orthogonality between orbitals must separately be formally forced. Techniques to force such orthogonality have been derived elsewhere,²⁻⁵ and those results will be used here. We may remove the self-exchange term by requiring each orbital ϕ_j to satisfy the equation

$$F_j \phi_j = \epsilon_j \phi_j, \quad (6)$$

where

$$F_j = F - J_j + K_j. \quad (7)$$

A naive approach to the asymptotic problem for Hartree-Fock orbitals leads to the assumption that when an electron in orbital j is removed from a neutral atom at a large distance, the relevant one-particle equation should be

$$H\phi_j = \epsilon_j \phi_j, \quad (8)$$

where

$$H = -\frac{1}{2}\nabla^2 - 1/r. \quad (9)$$

For Eq. (8) to hold asymptotically, $K_i \phi_j$ must go to zero faster than ϕ_j/r as r goes to infinity, for all i ; i. e.,

$$(r/\phi_j) K_i \phi_j \xrightarrow{r \rightarrow \infty} 0 \text{ for all } i. \quad (10)$$

The HMS paper has shown that Eq. (10) does not

hold for atoms with both s and p orbitals unless the dipole integral between s and p orbitals vanishes identically.

One method which will ensure that Eq. (10) holds is to construct a modified exchange operator K_i^* such that exchange only occurs within a finite "sphere of influence" of the electrons. Consider two particles labeled k and l which interact if particle l is within k 's sphere of influence (call this a kl interaction) or if k is within l 's sphere of influence, i. e., an lk interaction. The sphere of influence of particle l will be defined by a radius given by $n/(-2\epsilon_l)^{1/2}$, i. e., n times the DeBroglie wavelength of particle l . A similar definition is made for particle k .

If particle l is placed at a distance r_{kl} from particle k , there will be an interaction with k if $r_{kl} \times (-2\epsilon_k)^{1/2}/n < 1$; and no interaction if this ratio is greater than 1. Similarly, if one considers particle l , its interaction with k will be significant if $r_{kl} \times (-2\epsilon_l)^{1/2}/n < 1$. The exchange term is a mutual interaction and will occur in the framework if

$$r_{kl} [(-2\epsilon_k)^{1/2} + (-2\epsilon_l)^{1/2}]/n < 2. \quad (11)$$

Diagrammatically the problem can be seen in Figs. 1(a)-1(c). If particle l has a larger sphere of interaction than k , and k and l are arranged as in Fig. 1(a), then l will "see" or interact with k and k will "see" l . In Fig. 1(b), l will "see" k but k will not "see" l . In Fig. 1(c) there will be no interactions between particles k and l .

An exchange operator which satisfies the foregoing criterion is

$$K_k^* \phi_l = \phi_k(1) \int \phi_k^*(2) \phi_l(2) \{[1-u]/r_{12}\} dv(2), \quad (12)$$

where

$$u = u(x) = \begin{cases} 0 & \text{if } x \leq 0 \\ 1 & \text{if } x > 0 \end{cases}, \text{ with } x = r_{12} - r_{12}^0. \quad (13)$$

With this operator K_k^* the "sphere-of-influence" idea is regarded as a gross effect and an average interaction radius defined by r_{12}^0 is used for all orbitals. This simplification should not substantially change the results to follow.

Other types of exchange cutoffs have been suggested in defining the sphere of influence. Suggested in the HMS paper was the use of an

$$r_{12}^{-1} e^{-\alpha|(r_1^2 + r_2^2)}$$

potential in the exchange operator, which accomplishes a cutoff regardless of the size α if a Slater-type orbital (STO) basis set is used for the expansion of the Hartree-Fock orbitals. Another possibility is the use of $r_{12}^{-1} e^{-\alpha|r_1^2}$ in place of $1/r_{12}$ in the exchange potential. Both of these suggestions could in principle easily be used; however, the difficulties in evaluating the modified exchange integrals between STO basis elements is great. The exchange cutoff we have chosen here acts as a cutoff

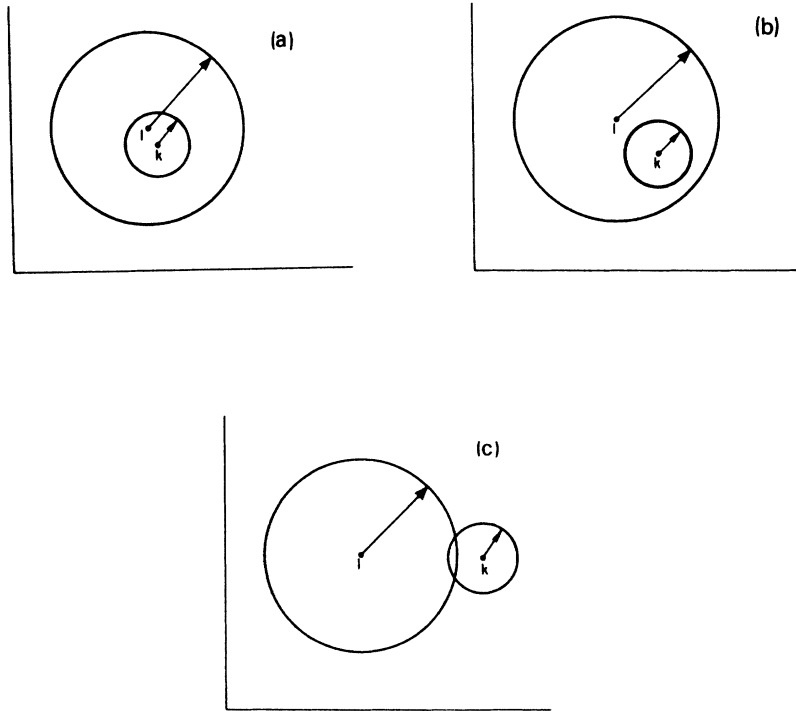


FIG. 1. (a) Particles k and l interact, (b) particle l "sees" k but k does not "see" l , (c) particles k and l do not interact.

potential regardless of the expansion basis set chosen and is much easier to deal with computationally. Results obtained with alternative cutoff schemes probably would agree.

III. PSEUDO-HARTREE-FOCK EQUATIONS

The pseudo-Hartree-Fock equations to be solved in the present sphere-of-influence framework are given by

$$F_j^* \phi_j^* = \epsilon_j \phi_j^*, \quad (14)$$

where

$$F_j^* = -\frac{1}{2} \nabla^2 - Z/r + \sum_{i \neq j} (2J_i - K_i^*) + J_j. \quad (15)$$

K_i^* and J_i are defined by Eqs. (12) and (5a), respectively. Two limits of the operator F_j^* should be noted. When r_{12}^0 approaches infinity it is seen that

$$F_j^* \rightarrow F_j, \quad (16)$$

where F_j is given by Eq. (7). When $r_{12}^0 \rightarrow 0$, on the other hand, the operator F_j^* goes to the Hartree operator, i. e., $K_i^* = 0$.

Since the operator given in Eq. (15) is not derivable from a particular wave function using a fixed Hamiltonian, there occurs an ambiguity in the definition of the total energy. The total energy, given by the formula

$$E = \sum_i (I_i + \epsilon_i^*), \quad (17)$$

where

$$I_i = \langle \phi_i | -\frac{1}{2} \nabla^2 - Z/r | \phi_i \rangle, \quad (18)$$

will in general be different from that given by

$$E = \sum_i I_i + \sum_{i < j} (2J_{ij} - K_{ij}). \quad (19)$$

Since our purpose is to derive orbitals which satisfy the long-range behavior given by Eq. (2), but not to otherwise perturb the conventional scheme, the formula we choose for the total energy is Eq. (19). This means that the orbitals are calculated by use of Eq. (14), but then the total wave function is constructed from a Slater determinant of these orbit-

TABLE I. Hartree-Fock energies for Ne using exchange cutoff.^a

r_{12}^0	$-E_{\text{Total}}$	$-\epsilon_{1s}$	$-\epsilon_{2s}$	$-\epsilon_{2p}$
∞	128.546186	32.77334	1.93050	0.85098
10.0	128.546186	32.77334	1.93050	0.85098
5.0	128.546186	32.77331	1.93049	0.85094
3.5	128.546163	32.77711	1.93385	0.85300
3.0	128.545962	32.78616	1.94241	0.85829
2.5	128.544937	32.80806	1.96721	0.87242
2.0	128.543077	32.83900	2.02435	0.89929
1.5	128.543970	32.82184	2.10911	0.92391
1.0	128.529632	32.65340	2.09293	0.89697
0.5	128.530155	32.63314	1.70226	0.76979
0.0	128.475935	32.97038	1.41183	0.67135

^aSee text, especially Eq. (15). When $r_{12}^0 = \infty$, the wave function is the Hartree-Fock function; when $r_{12}^0 = 0$, the wave function is the Hartree function.

als and the energy computed from the usual expectation value formula. Therefore, even as r_{12}^0 goes to zero, the total energy will be greater than the exact Hartree-Fock energy and will not go to the Hartree energy for the system. In this limiting case, our prescription is equivalent to solving the Hartree equations for the orbitals and then using these orbitals to construct an approximate Hartree-Fock wave function.

IV. RESULTS

In Table I are given the total and orbital energies for the Ne atom as a function of the exchange cutoff parameter r_{12}^0 . The $1s$ Hartree-Fock orbital is a linear combination of two $1s$ and one $2s$ STO. The STO with the smallest nonlinear parameter, call this ξ_{1s} ,⁶ governs the long-range behavior [Eq. (2)], and $\xi_{1s} \sim (-2\epsilon_{1s})^{1/2}$. The $2s$ Hartree-Fock orbital is a linear combination of the STO used in the description of the $1s$ orbital and two additional $2s$ STO. The additional $2s$ STO with the smallest nonlinear parameter ξ_{2s} governs the long-range behavior of the $2s$ orbital and $\xi_{2s} \sim (-2\epsilon_{2s})^{1/2}$. The $2p$ Hartree-Fock orbital is a linear combination of four $2p$ STO with the STO having the smallest nonlinear parameter $\xi_{2p} \sim (-2\epsilon_{2p})^{1/2}$ governing the asymptotic behavior of the $2p$ orbital.

Initially the linear and nonlinear parameters for a given r_{12}^0 are chosen as those used for the Hartree-Fock orbital ($r_{12}^0 = \infty$) given earlier.⁵ The pseudo-Hartree-Fock equations are then solved in the nested

TABLE II. Wave functions for selected values of r_{12}^0 for Ne.

r_{12}^0	ξ_{1s}	\bar{c}_{1s}	\bar{c}_{2s}	\bar{c}_{2p}
	ξ_{2s}			
3.0	8.09769	0.07397	0.00214	0.01726
	1.97104	-0.24267	0.01717	0.34759
	1.31025	1.14321	-0.30931	0.58380
		•••	0.77103	0.15278
		•••	0.32657	
2.0	8.10420	0.07415	0.00852	0.01749
	2.01221	-0.24098	0.03100	0.34648
	1.34137	1.14151	-0.31914	0.57521
		•••	0.72498	0.16208
		•••	0.36749	
1.0	8.08132	0.07136	0.01754	0.01825
	2.04601	-0.25098	0.02393	0.32982
	1.33947	1.15294	0.27366	0.64138
		•••	-0.84984	0.09790
		•••	-0.24992	
0.0	8.12039	0.06918	0.02727	0.01373
	1.68037	-0.24605	0.05581	0.33800
	1.15877	1.15020	0.21554	0.56234
		•••	-0.79117	0.20814
		•••	-0.34034	

TABLE III. Hartree-Fock wave function and expectation values for Ne.^{a,b}

$E_{\text{Total}} = -128.546186$		$E_{\text{HF}}^8 = -128.546980$	
$\epsilon_{1s} = -32.77334$		$\epsilon_{2s} = -1.93050$	
		$\epsilon_{2p} = -0.85098$	
S Basis			
n_i	ξ_i	$c_{1s}(r_{12}^0 = \infty)$	$c_{2s}(r_{12}^0 = \infty)$
1	14.39380	0.07385	-0.00115
2	8.80690	-0.24322	0.01031
1	8.09609	1.14380	-0.30328
2	3.43120	•••	0.78600
2	1.96498	•••	0.31302
P Basis			
n_i	ξ_i	$c_{2p}(r_{12}^0 = \infty)$	
2	9.35500	0.01753	
2	4.45450	0.34561	
2	2.27170	0.58940	
2	1.30459	0.14824	
	$\langle 1s r 1s \rangle = 0.15746$	$\langle 1s r 2s \rangle = 0.04457$	
	$\langle 2s r 2s \rangle = 0.89367$	$\langle 2p r 2p \rangle = 0.96570$	
	$\langle 1s^2 r_{12} 1s^2 \rangle = 0.23006$	$\langle 2s^2 r_{12} 2s^2 \rangle = 1.27133$	
	$\langle 1s^2 r_{12} 2s^2 \rangle = 0.91009$	$\langle 2s^2 r_{12} 2p^2 \rangle = 1.33674$	
	$\langle 1s^2 r_{12} 2p^2 \rangle = 0.98149$		
	$\langle 2p_x^2 r_{12} 2p_x^2 \rangle = 1.38271$	$\langle 2p_x^2 r_{12} 2p_y^2 \rangle = 1.41212$	

^a Wave function of Ref. 5 and present paper with $r_{12}^0 = \infty$.

^b The expectation values are defined as

$$\langle a | r | b \rangle = \int a^*(1) r_1 b(1) dv(1),$$

$$\langle a^2 | r_{12} | b^2 \rangle = \iint a^*(1) a(1) r_{12} b^*(2) b(2) dv(1) dv(2).$$

The usual symmetry relations hold, viz.,

$$\langle a^2 | r_{12} | b^2 \rangle = \langle b^2 | r_{12} | a^2 \rangle,$$

$$\langle p_x^2 | r_{12} | p_x^2 \rangle = \langle p_y^2 | r_{12} | p_y^2 \rangle = \langle p_z^2 | r_{12} | p_z^2 \rangle,$$

$$\langle p_x^2 | r_{12} | p_y^2 \rangle = \langle p_x^2 | r_{12} | p_z^2 \rangle = \langle p_y^2 | r_{12} | p_z^2 \rangle.$$

A p orbital without subscript indicates that either a p_x , p_y , or p_z orbital gives equivalent results.

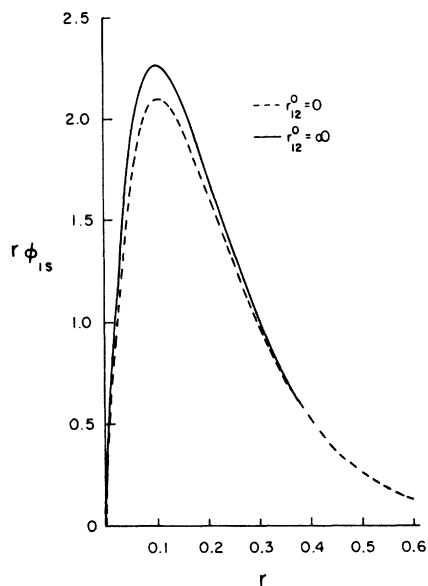
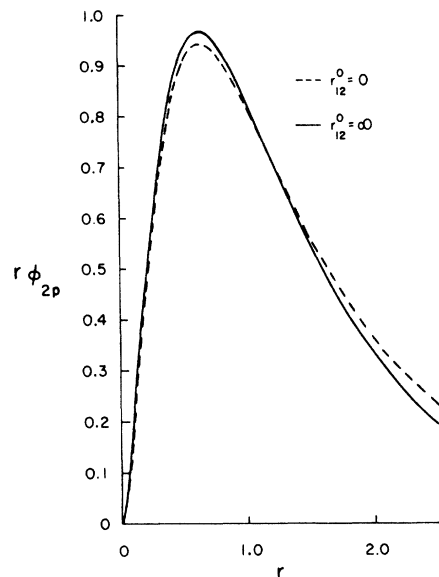
basis framework² for a new set of linear parameters. If the new orbital energies ϵ_i obtained are each within chemical accuracy (0.002 a.u.) of $-\frac{1}{2} \xi_i^2$, then the iteration procedure is stopped; otherwise, the nonlinear parameters ξ_i are changed and the iteration procedure is continued.

The best wave functions obtained for selected values of r_{12}^0 are given in Table II. The ξ_i and linear parameters are listed in this table. The full Hartree-Fock wave function is listed in Table III along with expectation values of r and certain r_{12} expectation values which should give an indication of the effective r_{12} regions for the various orbitals. In Figs. 2-4, radial graphs of $r \phi_{1s}$, $r \phi_{2s}$, and $r \phi_{2p}$, respectively, are plotted for $r_{12}^0 = 0$ and $r_{12}^0 = \infty$.

Certain quantities $\Delta\epsilon_i$, defined by

$$\Delta\epsilon_i(r_{12}^0) = \epsilon_i(r_{12}^0) - \epsilon_i(r_{12}^0 = \infty), \quad (20)$$

are convenient measures of changes in orbitals as a function of the cutoff parameter. Figure 5 exhibits plots of $\Delta\epsilon_{1s}$, $\Delta\epsilon_{2s}$, and $\Delta\epsilon_{2p}$ for values of r_{12}^0 from 0.0 to 4.0 a.u. One sees that there is a nonmonotonicity of the breakdown of the orbitals as

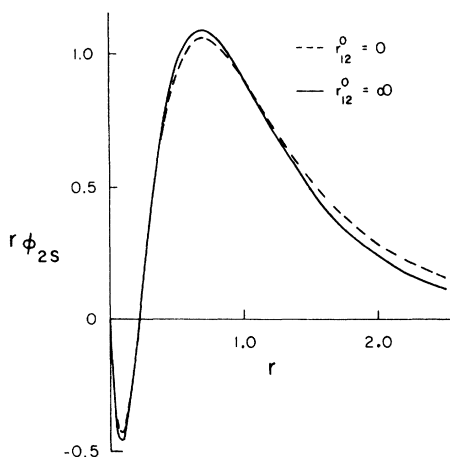
FIG. 2. Radial graph of $r\phi_{1s}$ for Ne. Atomic units.FIG. 4. Radial graph of $r\phi_{2p}$ for Ne. Atomic units.

one goes from the Hartree-Fock to the Hartree case.

In Fig. 6, ΔE , defined as

$$\Delta E(r_{12}^0) = E_{\text{Total}}(r_{12}^0) - E_{\text{Total}}(\infty), \quad (21)$$

is plotted as a function of r_{12}^0 . E_{Total} is calculated by means of Eq. (19). We see that r_{12}^0 can be quite small – on the order of 1.5 a. u. – and still chemical accuracy is maintained in the total energy. The first oscillation in the difference curve of Fig. 6 corresponds to the region where the $\Delta\epsilon_i$'s all have a minimum. The second oscillation corresponds to the region where $\Delta\epsilon_{1s}$ is rapidly decreasing and $\Delta\epsilon_{2s}$ and $\Delta\epsilon_{2p}$ are rapidly increasing. Some shift in balance between these two factors seems to have oc-

FIG. 3. Radial graph of $r\phi_{2s}$ for Ne. Atomic units.

curred to produce the second oscillation in the ΔE_{Total} curve.

The calculations performed on Ne essentially used the Roothaan and Bagus⁷ prescription except for modifications in the exchange integrals and nested basis procedures.

V. CONCLUSIONS

The results of this study indicate, as expected, that exchange cutoff becomes energetically important only as r_{12}^0 becomes small. Therefore, although Eq. (1) is the correct asymptotic equation for Hartree-Fock orbitals, no key energy contributions are connected with this fact.

One is therefore allowed to redefine an independent-particle approach without sacrificing energy. One in fact may think of an electron which is removed from an atom as somehow distinguishable from the other electrons in the ion – distinguishable by the fact of separation. This electron in some sense sees the ion as just a classical positive charge if the separation distance is large enough, and, therefore, in this context, exchange effects may be neglected.

Conversely, the implications of this study are that one need not be concerned with the formal Hartree-Fock behavior as given in Eq. (1), since this behavior is energetically unimportant. The formal behavior of Hartree-Fock orbitals, as distinguished from their exchange-cutoff counterparts, is only important in regions relatively near the nucleus, so that the exchange problem at long range is in this sense a moot question.

One might seek a means for constraining the Har-

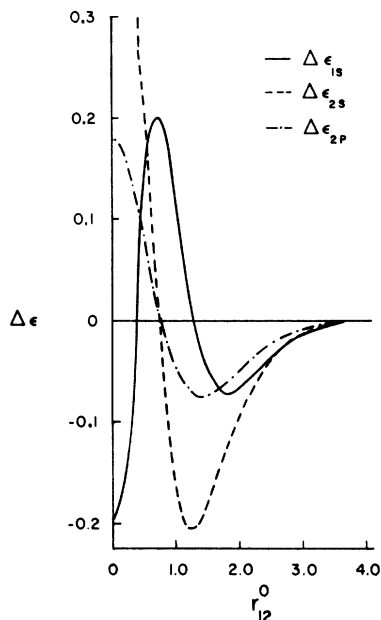


FIG. 5. Plot of $\Delta\epsilon_i$ versus r_{12}^0 for Ne. Atomic units.

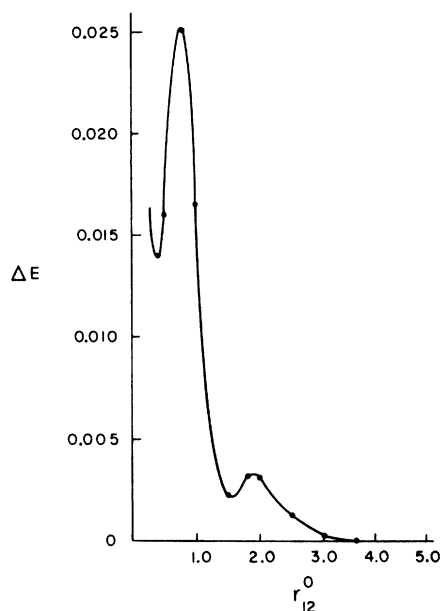


FIG. 6. Plot of ΔE versus r_{12}^0 . Atomic units.

tree-Fock equations to have the behavior given by Eq. (2) in all cases. One method which would work for the first-row atoms is to force the dipole integral between s and p orbitals to be identically zero. However, such a rigorous constraint would force at least one spurious node to occur, probably a radial node in the $2p$ orbital. This would imply a ground-state configuration for Ne of the type $[1s^2 2s^2 3p^6]$. Such a configuration very likely would be unsatisfactory energetically. Also, the introduction of spurious nodes would defeat the purpose of the nested basis procedure. This procedure was an operational means of eliminating the extra nodes found in the standard Clementi-type wave functions⁸ and instead calculating wave functions which have Sturm-Liouville-type model properties.

Alternatively, perhaps some nonlinear constraint based upon Eq. (2) could be directly applied to the variation procedure. However, a systematic approach to handling such nonlinear constraints and the reduction of the resulting equations to an eigen-

vector-type equation has not yet been found.

The apparent ambiguity in the definition of the total energy formula occurs since as r_{12}^0 goes from zero to infinity in Eq. (14), the modified Fock operator varies smoothly between the Hartree operator (which variationally implies a simple product form for the total wave function) and the Hartree-Fock operator (which variationally implies an antisymmetric product for the total wave function). If a smooth limiting procedure for the total wave function could be devised which took a Hartree-Fock wave function to a Hartree wave function, it would be possible to variationally construct an operator of the type given by Eq. (14).

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