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Bare-Nucleus and Screened-Nucleus Perturbation Theory for He₂

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In the bare-nucleus perturbation theory, where the full interelectronic repulsion is taken as the perturbing part of the Hamiltonian, determination of the first-order wavefunction for a closed-shell system reduces to a set of two-electron problems. Only in the evaluation of the energy do three-electron integrals appear. One can thus produce a correlated wavefunction (containing interelectronic distances explicitly) without evaluation of three-electron integrals as arise in the variational method. After a review of the necessary formulas, we present calculations for He₂. The convergence of the energy series is disappointing. However, the same formalism can be used when any one-electron local operator is taken as zero-order Hamiltonian. In particular we present screened-nucleus calculations, the zero-order Hamiltonian corresponding to noninteracting electrons moving in the field of nuclei of charge 1.5. Here, our energy through second order is as good as the best variational calculations.

I. INTRODUCTION

Our object in this article is to show that first-order perturbation theory may be used to calculate correlated electronic wavefunctions for small molecules with more than two electrons. We test two methods for the species He₂ with internuclear distance near $R=1.0a_0$. It was shown by Sinanoğlu[1] that the determination of the first-order wavefunction, from which the energy through third order may be calculated, reduces to a set of two-electron problems when the full interelectronic repulsion is taken as perturbation (bare-nucleus perturbation theory). The breakdown into pairs no longer holds in the next order of perturbation theory. At present, the only calculations using the bare-nucleus theory for a system of more than two electrons are for atoms. For Li, good results were obtained by Seung and Wilson[2a] Chisholm and Dalgarno,[2b] Layzer et al.,[2c] and Chisholm et al.[2d] Linderberg[3] has evaluated part of the second-order energy for various states of two-, four-, and six-electron atomic systems, obtaining good total energies in many cases. Here we first perform a calculation of the energy of the ground state of He₂ and obtain discouraging results. However, the bare-nucleus method is only the first in a hierarchy of methods which can give much better results while maintaining the advantages of the formalism. As we show below, even the most obvious improvement suffices to produce extremely accurate energies for the four-electron homonuclear diatomic.

At present, the most common means for introducing interelectronic correlation is interaction of configurations.[4] As is well known, slow convergence necessitates the use of a large number of determinants, with attend-ant computational difficulties. It must be noted that the use of natural orbitals[5] may alleviate the problem. A better way of taking care of the correlation is the use of wavefunctions explicitly involving the interelectronic distances, such as have been so successful for two-electron problems.[6] Schwartz[7] has indicated some of the reasons for the superiority of expansions in r_{12} to configuration interaction. The difficulty here, when one is concerned with more than two electrons, is the evaluation of the multi-electron integrals that arise. Some progress is being made on these for atoms,[8] but the accurate evaluation of many-center three- and four-electron integrals has so far proved too difficult. One cannot tolerate large errors in these integrals in a variational calculation because such errors may propagate up in an unknown way. As will appear later, the three-electron integrals appear in the present perturbation calculations only in the second-order energy, not in the wavefunction, so that, if one can estimate the errors in these integrals, one also knows the error in the final result for the energy. If, in addition, the integrals are themselves small, fairly large errors may be tolerated, so that relatively crude numerical methods will suffice for their calculation.

In a perturbation treatment, we are free to partition the molecular electronic Hamiltonian into perturbing and unperturbed parts as we like. Perturbation theory is simply a means of going from a problem we can solve to one we cannot. If $\mathbf{H}_0$, the unperturbed part, is one-electron, the zero-order wavefunctions may be accurately calculated or approximated, and we consider any one-electron Hamiltonian soluble. For any such partition, the three-electron integrals enter as indicated above. However, the choice of $\mathbf{H}_0$ determines how quickly the perturbation series $(E=E^{(0)}+E^{(1)}+E^{(2)}+\cdots)$ converges. Since we will stop with the second-order energy, this is very important for us.

[1] O. Sinanoğlu, Phys. Rev. **122**, 493 (1961).

[2] (a) S. Seung and E. B. Wilson, Jr., J. Chem. Phys. **47**, 5343 (1967); (b) C. D. H. Chisolm and A. Dalgarno, Proc. Roy. Soc. (London) **A292**, 264 (1966); (c) D. Layzer, Z. Horak, M. N. Lewis, and D. P. Thompson, Ann. Phys. (N.Y.) **29**, 101 (1964); (d) C. D. H. Chisolm, A. Dalgarno, and F. R. Innes, Phys. Rev. **60** (1968). This last is on the $1s^22p^2P$ state, the others on the ground state.

[3] J. Linderberg, J. Mol. Spectry. **9**, 95 (1962).

[4] J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1963), Vol. 1.

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[6] E. A. Hylleraas, Advan. Quantum Chem. **1**, 1 (1964); H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[7] C. S. Schwartz, Phys. Rev. **126**, 1015 (1962).

[8] J. H. Karl, J. Chem. Phys. **46**, 4219 (1967), and references therein.

The best one-electron Hamiltonian in terms of making the perturbing Hamiltonian small would be the Hartree–Fock. We have chosen not to use it because it does not allow the deferral of the three-electron integrals to the end of the calculation. It is frequently said that the Hartree–Fock Hamiltonian permits the separation of the multi-electron problem into a set of two-electron problems. This is true in a formal sense only. As pointed out by Geller et al.,[9] the nonlocal nature of the Hartree–Fock Hamiltonian effectively makes the determination of a pair function into a three-electron problem. In contrast to this, the use of the bare nucleus or other *local* Hamiltonian as unperturbed Hamiltonian leads to true two-electron equations for the first-order wavefunction. However, the second-order energy includes three- and four-electron contributions and necessitates the evaluation of three-electron integrals.

With Hartree–Fock as starting point, the second- and higher-order energy terms would be the correlation energy, according to the current definition[10] of this term. Naturally, this does not obtain in the present treatment. Here, there are both one-electron and two-electron corrections in the first-order wavefunction, while the former vanish when the zero-order function is taken as Hartree–Fock. On the other hand, as emphasized by Sinanoğlu,[1] the bare-nucleus calculation corresponds to a superposition of well-defined physical problems. Conkie[11] has emphasized that, considering more and more terms in the perturbation expansions for several choices of H_0, an inferior choice tends to catch up with a better one.

For two-electron systems, the bare-nucleus perturbation theory gives good results. Calculations have been performed for the ground states of H_2[12] and HeH^+,[13] but the Hartree–Fock perturbation calculations are not available for these systems. A comparison may be made for the He ground state: the calculations of Knight and Scherr[14] with a bare-nucleus Hamiltonian yield $E^{(0)} = -4$, $E^{(1)} = 5/4$, $E^{(2)} = -0.15767$, $E^{(3)} = 0.00435$ for an energy of -2.90332 a.u., while the perturbed Hartree–Fock calculations of Byron and Joachain[15] yield $E^{(0)} + E^{(1)} = -2.8617$, $E^{(2)} = -0.0373$, $E^{(3)} = -0.0038$ for an energy of -2.9028 a.u. (The true energy is -2.9038.) Here, the Hartree–Fock is not

better than bare nuclei in third order, and the two differ from one another (and from the exact) by only $\frac{1}{2}$ kcal in second order. (Results from higher-order perturbation theory have been reported for both cases, but do not concern us here.) For Li, Seung and Wilson[2a] report $E^{(0)} = -10.125$, $E^{(1)} = 3.0684$, $E^{(2)} = -0.4083$, and $E^{(3)} = -0.0077$ a.u. A Hartree–Fock calculation[16] gives $E_{HF} = E^{(0)} + E^{(1)} = -7.4327$. It is expected that the Hartree–Fock starting point becomes more advantageous vis à vis the bare nucleus for the present four-electron problem, since the latter does not take into account the screening of the outer electrons by the inner ones.

Between the bare nucleus and the Hartree–Fock there is a hierarchy of one-electron Hamiltonians which can be used for H_0. We may order them by the approach of their lowest four-electron eigenfunctions to the true eigenfunction of H, as judged by the expectation values of H calculated with these functions. We consider local zero-order Hamiltonians only. The obvious first choice in investigating improvements on the bare nucleus starting point is "screened nuclei," or the use of effective charges. The zero-order Hamiltonian corresponds to noninteracting electrons moving in the Coulombic field of nuclei of some charge Z, which may be chosen to minimize $\langle \Phi^{(0)} \mid H_0 + H_1 \mid \Phi^{(0)} \rangle = E^{(0)} + E^{(1)}$. The calculation for the He atom ($Z = 27/16$) is familiar from text books,[17] where the physics involved is discussed.

For H_2, at $R = 1a_0$, a charge of 0.8 gives $E^{(0)} = -1.9897$, $E^{(1)} = -0.0887$, $E^{(2)} = -0.0525$, $E^{(3)} = 0.0082$. The bare-nucleus expansion[12a] has $E^{(0)} = -2.90357$, $E^{(1)} = 0.89006$, $E^{(2)} = -0.11819$, $E^{(3)} = 0.00787$, and is seen to catch up at third order. We demonstrate below how the screened nuclei starting point is used for a multielectronic system, and that it is a great improvement for He_2 over bare nuclei. For a calculation with four or more electrons, calculation of $E^{(3)}$ seems too difficult—it is already a formidable task for the three-electron atom[2]—so that we stop with $E^{(2)}$. Note that the four-electron problem contains all the complications that can arise in applying this method to N electrons, except for degeneracy due to spatial symmetry.

We consider first the bare-nucleus calculations. Sections II and IV give the necessary formulas, Sec. III discusses the zero-order wavefunction and the pair functions. The energies obtained are in Sec. IV. In Sec. V we present the screened-nuclei calculation. The formalism of Sec. II and IV can be used here, too. Results for screened nuclei and final discussion are in Sec. VI.

II. FIRST-ORDER WAVEFUNCTION

The Hamiltonian for an N-electron system is divided into two parts for treatment by perturbation theory.

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[10] P.-O. Löwdin, Advan. Chem. Phys. **2**, 207 (1959).

[11] W. R. Conkie, Can. J. Phys. **43**, 102 (1965); J. Chem. Phys. **43**, 3408 (1965).

[12] (a) R. L. Matcha, University of Wisconsin Theoretical Chemistry Institute Rept. WIS-TCI-129 (October 1965); R. L. Matcha and W. Byers Brown, J. Chem. Phys. **48**, 74 (1968); (b) B. Kirtman and D. R. Decious, J. Chem. Phys. **44**, 830 (1966); **48**, 3133 (1968); (c) Dvořáček and Horák [J. Chem. Phys. **47**, 1211 (1967)] have used as zero-order Hamiltonian that for a bare nucleus of charge Z at the molecular midpoint, calculating first-order corrections due to the one-electron potential as well as $V_{\gamma_{12}}$.

[13] L. J. Bartolotti and J. Goodisman, J. Chem. Phys. **49**, 4237 (1968).

[14] R. E. Knight and C. W. Scherr, Phys. Rev. **128**, 2675 (1962).

[15] F. W. Byron and C. J. Joachain, Phys. Rev. **146**, 1 (1966).

[16] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960).

[17] L. Pauling and E. Bright Wilson, Jr., *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., New York, 1935), Secs. 26b, 29c. H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), Sec. 7d.

The unperturbed Hamiltonian is

$$\mathbf{H}_0 = \sum_{i=1}^{N} h_i^0, \tag{1}$$

where h_i^0 includes the kinetic energy and nuclear attraction operators for electron i. From the spin orbitals which are eigenstates of h_i^0,

$$h_i^0 \lambda_j(i) = \epsilon_j^0 \lambda_j(i) \tag{2}$$

we may obtain eigenstates of $\mathbf{H}_0$ as determinants

$$\Phi^{(0)} = \mathscr{A}\{\lambda_1(1)\lambda_2(2)\cdots\lambda_N(N)\}, \tag{3}$$

$$\mathbf{H}_0 \Phi^{(0)} = E^{(0)} \Phi^{(0)}, \tag{4}$$

$$E^{(0)} = \sum_{j=1}^{N} \epsilon_j^0. \tag{5}$$

Here, $\mathscr{A}$ is the normalized antisymmetrizer,

$$\mathscr{A} = (N!)^{-1/2} \sum_P (-1)^P P, \tag{6}$$

where P is a permutation of N particles, so that $\Phi^{(0)}$ is normalized to unity when the λ_i are orthonormal. We will discuss here only the case where $\Phi^{(0)}$ is a nondegenerate state formed by doubly occupying $n = \frac{1}{2}N$ orbitals. Then $\lambda_1 = \phi_1 \alpha$, $\lambda_2 = \phi_1 \beta$, $\lambda_3 = \phi_2 \alpha, \cdots$, $\lambda_N = \phi_n \beta$. We take all functions as real.

The perturbing term in the Hamiltonian is the interelectronic repulsion

$$\mathbf{H}_1 = \sum_{i<j=1}^{N} g_{ij}, \qquad g_{ij} = 1/r_{ij}. \tag{7}$$

The first-order energy is given by the familiar expression

$$E^{(1)} = \langle \Phi^{(0)} | \mathbf{H}_1 | \Phi^{(0)} \rangle = \sum_{i<j=1}^{N} (\bar{J}_{ij} - \bar{K}_{ij}), \tag{8}$$

where $\bar{J}_{ij}$ and $\bar{K}_{ij}$ are Coulomb and exchange integrals between spin orbitals λ_i and λ_j, the latter vanishing when the spins of λ_i and λ_j do not match. In terms of the orbital functions

$$E^{(1)} = \sum_{i<j=1}^{n} (4J_{ij} - 2K_{ij}) + \sum_{i=1}^{n} J_{ii} \tag{9}$$

with

$$J_{ij} = \int d\tau_1 d\tau_2 \phi_i(1)\phi_j(2)(1/r_{12})\phi_i(1)\phi_j(2), \tag{10a}$$

$$K_{ij} = \int d\tau_1 d\tau_2 \phi_i(1)\phi_j(2)(1/r_{12})\phi_j(1)\phi_i(2). \tag{10b}$$

Note that $\bar{J}$ and $\bar{K}$ have subscripts corresponding to spin–orbital indices, J and K subscripts corresponding to orbital indices.

It is interesting to note that $E^{(1)}$ may be written as a sum over normalized pure spin-state pairs. Introducing

the two-particle antisymmetrizer

$$\mathscr{B}_{ij} = (1/\sqrt{2})(1 - P_{ij}) \tag{11}$$

we define

$$u_{ij}^0 \equiv \mathscr{B}_{12}\{\lambda_i(1)\lambda_j(2)\}. \tag{12}$$

We introduce the abbreviations

$$\mathscr{S}(i,j) = 2^{-1/2}[\alpha(i)\beta(j) - \beta(i)\alpha(j)], \tag{13}$$

$$\mathscr{T}_0(i,j) = 2^{-1/2}[\alpha(i)\beta(j) + \beta(i)\alpha(j)], \tag{14}$$

$$\mathscr{T}_+(i,j) = \alpha(i)\alpha(j), \tag{15}$$

$$\mathscr{T}_-(i,j) = \beta(i)\beta(j), \tag{16}$$

for the two-electron spin function. If $i = 2k-1$, $j = 2k$, we get an intrashell pair

$$u_{2k-1,2k}^0 = \phi_k(1)\phi_k(2)\mathscr{S}(1,2). \tag{17}$$

If i and j are both even or both odd, we get states belonging to the intershell triplet

$$u_{2k,2l}^0 = [\phi_k(1)\phi_l(2) - \phi_l(1)\phi_k(2)]2^{-1/2}\mathscr{T}_-(1,2), \tag{18}$$

$$u_{2k-1,2l-1}^0 = [\phi_k(1)\phi_l(2) - \phi_l(1)\phi_k(2)]2^{-1/2}\mathscr{T}_+(1,2). \tag{19}$$

Otherwise, we get a mixed pair which is broken down into a singlet and triplet. For instance, if $k < l$,

$$u_{2k-1,2l}^0 = 2^{-1/2}\{[\phi_k(1)\phi_l(2) + \phi_l(1)\phi_k(2)]/\sqrt{2}\}\mathscr{S}(1,2)$$
$$+ 2^{-1/2}\{[\phi_k(1)\phi_l(2) - \phi_l(1)\phi_k(2)]/\sqrt{2}\}\mathscr{T}_0(1,2). \tag{20}$$

To the expectation value of $1/r_{12}$, each intrashell pair (17) contributes J_{kk}, each intershell triplet (18), (19) $J_{kl} - K_{kl}$, and each mixed pair (20) $\frac{1}{2}[J_{kl} + K_{kl} + J_{kl} - K_{kl}]$. For the N-electron n-orbital problem, the $N(N-1)/2$ pairs include n intrashell pairs, $n(n-1)$ intershell triplets, and $n(n-1)$ mixed pairs, so the total contribution to the expectation value of $1/r_{12}$ is just Eq. (9).

The first-order wavefunction $\Phi^{(1)}$ of perturbation theory, from which the second- and third-order energies may be calculated, is the solution to

$$[\mathbf{H}_0 - E^{(0)}]\Phi^{(1)} + [\mathbf{H}_1 - E^{(1)}]\Phi^{(0)} = 0. \tag{21}$$

We now define, with Sinanoğlu,[1]

$$e_i \equiv h_i^0 - \epsilon_i^0, \tag{22}$$

$$m_{ij} \equiv -g_{ij} + \bar{J}_{ij} - \bar{K}_{ij}, \tag{23}$$

so (21) becomes:

$$\sum_{i=1}^{N} e_i \Phi^{(1)} = \frac{1}{2} \sum_{i \neq j=1}^{N} m_{ij} \mathscr{A}\{\lambda_1(1)\lambda_2(2)\cdots\lambda_N(N)\}. \tag{24}$$

The right-hand side of the equation being antisymmetric, $\Phi^{(1)}$ must be antisymmetric, and we put

$$\Phi^{(1)} = (1/\sqrt{2})\mathscr{A}X_1. \tag{25}$$

Sinanoğlu[1] has shown that X_1 may be written as a sum of terms, each of which differs from $\Phi^{(0)}$ by only

two electrons, thus:

$$X_1 = \sum_{i < j = 1} \left[\prod_{k=1}^{N} \lambda_k(k) \right] \frac{u_{ij}(i,j)}{\lambda_i(i)\lambda_j(j)}, \qquad (26)$$

where

$$(e_i + e_j) u_{ij}(i,j) = m_{ij} \mathfrak{B}_{ij} \{ \lambda_i(i) \lambda_j(j) \} = m_{ij} u_{ij}{}^0, \quad (27)$$

if $u_{ij}{}^0$ is an intrashell pair (singlet) or an intershell triplet. Then u_{ij} will be a product of space and spin parts, with the spin part the same as that of $u_{ij}{}^0$. Where λ_i and λ_j differ in both space and spin parts, there is a spin-exchange degeneracy which may be handled[1] by writing u_{ij} as a sum of singlet and triplet pairs. For instance,

$$u_{14}(1,4) = 2^{-1/2} [{}^3u_{14}(1,4) + {}^1u_{14}(1,4)] \qquad (28)$$

such that ${}^3u_{14}(1,4) = {}^3f_{12}(1,4) \mathfrak{J}_0(1,4)$ with

$$(e_1 + e_4){}^3f_{12}(i,j) = (J_{12} - K_{12} - g_{ij})$$
$$\times [\phi_1(i)\phi_2(j) - \phi_2(i)\phi_1(j)] 2^{-1/2} \quad (29)$$

and ${}^1u_{14}(1,4) = {}^1f_{1'}(1,4) \mathcal{S}(1,4)$ with

$$(e_1 + e_4){}^1f_{12}(i,j) = (J_{12} + K_{12} - g_{ij})$$
$$\times [\phi_1(i)\phi_2(j) + \phi_2(i)\phi_1(j)] 2^{-1/2}. \quad (30)$$

Here, the f's (spatial functions) are labeled by orbital indices, the u's by spin–orbital indices. The spatial function of the intershell triplet mentioned earlier in this paragraph also satisfies Eq. (29). We will assume there are no degeneracies other than those considered. A general derivation of the breakdown of the first-order wavefunction into pairs is given by Chisholm and Dalgarno.[2b]

To summarize, the first-order wavefunction is given by Eqs. (25) and (26) with the u_{ij} antisymmetric to interchange of electrons. $\Phi^{(1)}$ is a sum of $\frac{1}{2}N(N-1)$ terms, each of which is obtained from $\Phi^{(0)}$ by replacing on $u_{ij}{}^0$ by the corresponding u_{ij}. The spin functions and symmetry properties are the same for $u_{ij}{}^0$ and u_{ij} when $u_{ij}{}^0$ is an intershell triplet or an intrashell pair; the mixed pair (20), which is a sum of pure spin states, is replaced by the corresponding sum (28). This guarantees that $\Phi^{(1)}$ is a singlet.[18] Specializing to the four-electron case ($N=4$, $n=2$) we summarize the form of the pair functions

$$u_{12} = f_{11} \mathcal{S}, \qquad (31a)$$

$$u_{13} = {}^3f_{12} \mathfrak{J}_+, \qquad (31b)$$

$$u_{14} = 2^{-1/2}({}^3f_{12}\mathfrak{J}_0 + {}^1f_{12}\mathcal{S}), \qquad (31c)$$

$$u_{23} = 2^{-1/2}({}^3f_{12}\mathfrak{J}_0 - {}^1f_{12}\mathcal{S}), \qquad (31d)$$

$$u_{24} = {}^3f_{12} \mathfrak{J}_-, \qquad (31e)$$

$$u_{34} = f_{22} \mathcal{S}. \qquad (31f)$$

Thus, there are only four different pair functions to be

[18] H. J. Silverstone and O. Sinanoğlu, J. Chem. Phys. **46**, 854 (1967).

determined, each a solution to a two-electron problem. In fact, each pair calculation corresponds to a state of the $He_2{}^{2+}$ molecule–ion.

III. BARE-NUCLEUS PERTURBATION THEORY

The zero-order wavefunction is constructed from solutions to the bare-nucleus problem, Eq. (2). For the ground state of He_2, we require the two solutions to the $He_2{}^{3+}$ problem which give the lowest energy. At the internuclear distances of 1.0 and $0.7a_0$, these are the lowest σ_g and σ_u orbitals. As shown below, this may be ascertained by examining the orbital energies of $H_2{}^+$ given, for instance, by Bates et al.[19a] at an internuclear distance of $2.0a_0$

The one-electron two-center Coulomb problem is capable of direct solution,[19] although not in closed form. Instead of using these solutions, we construct variational approximations by taking linear combinations of the basis functions

$$U_i = \lambda^{m_i} \mu^{n_i} e^{-\alpha\lambda}, \qquad (32)$$

where λ and μ are the ellipsoidal coordinates, and α is chosen to minimize the energy. We have used these previously for bare-nucleus calculations on H_2.[20] As the number of basis functions increases, the calculated energy becomes less sensitive to α. In the pair functions, an exponential in $\alpha(\lambda_1 + \lambda_2)$ appears; for computational convenience, we chose the α in (32) to match that for the corresponding pair function. This necessitates several approximate forms, with different α's, for each bare-nucleus orbital. Those used for the He_2 calculation at $R = 1.0a_0$ are given in Table I.

The accuracy to which these represent the zero-order functions may be judged from the ratios

$$\int F(1,2)(h_1{}^0 + h_2{}^0)\lambda_i(1)\lambda_j(2)d\tau \Big/ \int F(1,2)\lambda_i(1)\lambda_j(2)d\tau$$

where $F(1,2)$ is arbitrary. For the exact zero-order function, these always equal the zero-order energy. Integrals of this kind are calculated in the course of the determination of the u_{ij}. Another check is comparison of calculated with exact energies, which have been published for several one-electron diatomic systems.[19]

For atoms, the bare-nucleus perturbation theory leads to the $1/Z$ expansion[21] of the energy (Z = nuclear charge) when a scaling transformation is introduced. For molecules, the use of the Born–Oppenheimer approximation means that the scaling of lengths and nuclear charges is associated with a change of internuclear distance. This enables us to use the zero-order wavefunctions determined for one system for a second if the second relates to the first by multiplication of all

[19] (a) D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) **A246**, 215 (1954); (b) D. R. Bates and T. R. Carson, Proc. Roy. Soc. (London) **A234**, 207 (1956); H. Wind, thesis, University of Utrecht, 1965.
[20] J. Goodisman, J. Chem. Phys. **48**, 2981 (1968).
[21] P.-O. Löwdin, Mol. Spectry. **3**, 46 (1959).

nuclear charges by a constant. In the present case, orbitals and energies determined for H_2^+ can be employed.

Suppose we have solved the one-electron problem for nuclear charges Z and internuclear distances R. With $\mathbf{T}$ the kinetic energy operator and $\mathbf{V}$ the electron-nuclear attraction operator,

$$[\mathbf{T}(r)+\mathbf{V}(r; Z, R)]\Psi(r; Z, R) = E_0(Z, R)\Psi(r; Z, R).$$
(33)

In the Born–Oppenheimer approximation, Z and R enter as parameters. We represent the set of electronic coordinates, in a coordinate system fixed in space, by r. Now we change to scaled coordinates: $r=\eta\rho$, $R=\eta P$. Clearly, $\mathbf{T}(r)=\eta^{-2}\mathbf{T}(\rho)$ and $\mathbf{V}(r; Z, R)=\eta^{-1}\mathbf{V}(\rho; Z, P)$. Multiplying all nuclear charges through by η would multiply $\mathbf{V}$ by η: if $Z'=\eta Z$, $\mathbf{V}(\rho; Z, P)=\eta^{-1}V(\rho; Z', P)$. Then

$$[\mathbf{T}(\rho)+\mathbf{V}(\rho; Z', P)]\Psi(\eta\rho; Z, \eta P)$$
$$=\eta^2 E_0(Z, \eta P)\Psi(\eta\rho; Z, \eta P), \quad (34)$$

which means that the one-electron eigenvalue equation for charges $Z'=\eta Z$ and internuclear distances $P=R/\eta$ is satisfied by the wavefunction satisfying (33) if we multiply all the electronic coordinates by η, the eigenvalue being multiplied by η^2. For example, the energy for He_2^{3+} at a distance P is four times that for H_2^+ at a distance $2P$.

TABLE I. Orbitals used for zero-order functions, $R=1.0$ a_0, bare nuclei.

A. Lowest (σ_g) orbital, exclusive of $\exp(-\alpha\lambda)$ factor

Exponential parameter	1.3	1.5
Function	Coefficient in orbital	
1	3.104016	3.116888
μ^2	1.338127	1.243743
μ^4	0.161815	0.211860
λ	0.369848	0.984145
$\lambda\mu^2$	0.012554	0.387194
λ^2	−0.245816	−0.120636
$\lambda^2\mu^2$	−0.023628	−0.025174
λ^3	0.039885	0.010412
λ^4	−0.002309	
Energy	−4.410534	−4.410535

B. Second (σ_u) orbital, exclusive of $\exp(-\alpha\lambda)$ factor

Exponential parameter	1.1	1.3
Function	Coefficient in orbital	
μ	−1.976405	−1.946382
μ^3	−0.273132	−0.267067
$\lambda\mu$	−1.601166	−2.061520
$\lambda\mu^3$	−0.196098	−0.249398
μ^5	−0.026146	−0.034100
$\lambda^2\mu$	0.224971	−0.087528
$\lambda^3\mu$	−0.021778	−0.024703
$\lambda^2\mu^3$	0.015066	−0.035679
$\lambda^4\mu$	0.001006	
Energy	−2.670137	−2.670137

We use ellipsoidal coordinates, which depend on the internuclear distance. On transforming these to space-fixed coordinates, scaling, and then transforming back to ellipsoidal coordinates, one finds that the functional form is unchanged. This may not be true for other coordinate systems. Thus, our orbitals for an internuclear distance of $1.0a_0$ are the H_2^+ orbitals for an internuclear distance of $2.0a_0$. The orbitals for $0.7a_0$ were in fact those previously obtained for H_2^+ at $1.4a_0$.

The pair equations for the space part of an intrashell pair are

$$(h_1^0+h_2^0-2\epsilon_i^0)f_{ii}(1, 2) = (-1/r_{12}+J_{ii})\phi_i(1)\phi_i(2)$$
(35)

and for the space part of an intershell triplet or singlet,

$$(h_1^0+h_2^0-\epsilon_i^0-\epsilon_j^0)^{3,1}f_{ij}(1, 2) =[-(1/r_{12})+J_{ij}\mp K_{ij}]$$
$$\times[\phi_i(1)\phi_j(2)\mp\phi_j(1)\phi_i(2)]/2^{1/2}. \quad (36)$$

The scaling transformation of the previous section, if applied to these equations, shows that the f_{ii} or f_{ij} may also be transferred between systems for which all nuclear charges are divided, and all internuclear distances multiplied, by a constant. Consider Eq. (35) or (36) in the form

$$[\mathbf{H}_0(r; Z, R)-E_0(Z, R)]\Psi^{(1)}(r; Z, R)$$
$$=[-(1/r_{12})+E_1(Z, R)]\Psi^{(0)}(r; Z, R),$$

where

$$E_1(Z, R)=\langle\Psi^{(0)}(r; Z, R)\mid 1/r_{12}\mid\Psi^{(0)}(r; Z, R)\rangle$$

for

$$\Psi^{(0)}(r; Z, R)$$

normalized. Here, r stands for the coordinates of both electrons. Putting $r=\eta\rho$, $R=\eta P$, $Z'=\eta Z$, we obtain

$$[\eta^{-2}H_0(\rho; Z', P)-\eta^{-2}E_0(Z', P)]\Psi^{(1)}(\eta\rho; Z, \eta P)$$
$$=[-(\eta\rho_{12})^{-1}+\eta^{-1}E_1(Z', P)]\Psi^{(0)}(\eta\rho; Z, \eta P). \quad (37)$$

Since $\Psi^{(0)}(\rho; Z', P)=\Psi^{(0)}(\eta\rho; Z, \eta P)$, we see that $\Psi^{(1)}(\rho; Z', P)$, the solution to (37), is $\eta^{-1}\Psi^{(1)}(\eta\rho; Z, \eta P)$, which was to be shown. Furthermore, the second-order energy for the two-electron problem is

$$\langle\Psi^{(0)}\mid 1/r_{12}-E_1\mid\Psi^{(1)}\rangle,$$

and one finds that $E_2(Z', P)=E_2(Z, R)$. We have already noticed that $E_0(Z', P)=\eta^2 E_0(Z, R)$ and $E_1(Z', P)=\eta E_1(Z, R)$. This is the beginning of the $1/Z$ expansion.

Thus, the pair functions for He_2 at $R=1.0a_0$ could be obtained from the first-order wavefunctions for the bare-nucleus treatment of various states of H_2 at $R=2.0a_0$. The f_{11} intrashell pair corresponds to the ground state ($^1\Sigma_g^+$) the $^3f_{12}$ intershell pair to the lowest triplet state ($^3\Sigma_u^+$), the $^1f_{12}$ intershell pair to the lowest ungerade singlet state ($^1\Sigma_u^+$) and the f_{22} intrashell pair to the lowest doubly excited state ($^1\Sigma_g^+$). Calculations

on the first three of these states using bare-nucleus perturbation theory have recently been performed,[20] and the same methods are used here for the first three pairs. The direct numerical solution of the pair equations has been discussed,[22] but here we employ a variational method. The first-order wavefunction is approximated by an expansion in a James–Coolidge-type basis set

$$\Psi^{(1)} = \sum_i c_i V_i,$$

where

$$V_i = (1 \pm P_{12})\lambda_1{}^{p_i}\mu_1{}^{q_i}\lambda_2{}^{r_i}\mu_2{}^{s_i}(2r_{12}/R)^{m_i}. \quad (38)$$

The expansion coefficients are chosen by the Hylleraas–Bethe–Salpeter variational principle[23] and satisfy

$$c = M^{-1}N, \quad (39)$$

where

$$M_{ij} = \langle V_i \mid H_0 \mid V_j \rangle - E_0 \langle V_i \mid V_j \rangle,$$

$$N_j = \langle V_j \mid H_1 \mid \Psi^{(0)} \rangle - E_1 \langle V_j \mid \Psi^{(0)} \rangle.$$

The basis functions used here for the first three pair functions were selected from the set used for H_2 at $R = 1.4a_0$ on the basis of their importance there, and are shown in Table II for $R = 1.0$. Comparisons with results obtained with larger basis sets[20] enable us to estimate the error in truncating the sets as we have done. We could also have used the pair functions determined for H_2 at $R = 1.4$ for He_2 at $R = 0.7$. As the size of the basis increases, one of the eigenvalues of M goes to zero. By eliminating the contribution of the corresponding eigenvector in the calculation of M^{-1}, we avoid numerical difficulties[20] and essentially orthogonalize the pair function u_{ij} to the zero-order wavefunction $u_{ij}{}^0$.

As in previous calculations,[20,24] all integrals needed for Eq. (39) were evaluated numerically. In the two-electron integrals, the integrations over the two angular variables were performed exactly, and crossed Gauss quadratures were used in the remaining four dimensions $(\lambda_1, \lambda_2, \mu_1, \mu_2)$. For nonsingular integrands, Gauss quadrature was used for μ_1 and μ_2 and Gauss–Laguerre quadrature for λ_1 and λ_2 (λ and μ are the sum and difference of distances from the nuclei, divided by the internuclear distance.) Where the integrand was singular, a change of variables was made on λ_1 and λ_2:

$$w = \lambda_2 + \lambda_1$$

$$v = (\lambda_2 - \lambda_1)/(\lambda_2 + \lambda_1),$$

and we integrated over the former with Gauss–Laguerre formulas and over the latter with Gauss formulas. Experiments with changing the numbers of quadrature points were performed to show that the coefficients in the first-order wavefunctions are precise to 3–4 decimals.

[22] V. McKoy and N. W. Winter, J. Chem. Phys. **48**, 5514 (1968).

[23] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One-and Two-Electron Atoms* (Academic Press Inc., New York, 1957).

[24] J. Goodisman, J. Chem. Phys. **41**, 3889 (1964); **43**, 3037 (1965).

TABLE II. Convergence of pair functions, bare nuclei, $R = 1\ a_0$.

A. $(\sigma_g)^2$ Intrashell $^1\Sigma_g^+$ pair, f_{11} exponential parameter $= 1.5$

Basis function

p	q	r	s	m	$\tilde{E}_2{}^a$	$\tilde{E}_3{}^a$	$2\langle 0 \mid V_0 \mid 1 \rangle^b$
0	0	0	0	0			
0	0	0	0	1	−0.0915	0.0069	0.51
0	1	0	1	0	−0.0985	0.0079	0.46
1	0	0	0	0	−0.1003	0.0076	0.56
2	0	0	0	0	−0.1030	0.0058	0.59
1	0	0	0	1	−0.1031	0.0054	0.59
0	0	0	0	2	−0.1050	0.0071	0.62
0	0	0	2	0	−0.1053	0.0073	0.64

B. $\sigma_g\sigma_u$ Intershell $^1\Sigma_u^+$ pair, $^1f_{12}$ exponential parameter $= 1.3$

Basis function

p	q	r	s	m	$\tilde{E}_2{}^a$	$\tilde{E}_3{}^a$	$2\langle 0 \mid V_0 \mid 1 \rangle^b$
0	0	0	1	0			
1	0	0	1	0	−0.0113	−0.0010	0.22
1	1	0	0	0	−0.0675	0.0032	0.94
0	1	0	0	1	−0.1180	0.0093	1.03
1	0	0	1	1	−0.1193	0.0112	1.03
0	2	0	1	0	−0.1204	0.0113	1.07
2	1	0	0	0	−0.1477	−0.0009	1.33
0	0	0	1	2	−0.1493	0.0016	1.34
2	0	0	1	0	−0.1500	0.0018	1.35
1	1	0	0	1	−0.1556	0.0004	1.35
2	1	1	0	0	−0.1561	0.0003	1.34

C. $\sigma_g\sigma_u$ Intershell $^3\Sigma_u^+$ pair, $^3f_{12}$ exponential parameter $= 1.3$

Basis function

p	q	r	s	m	$\tilde{E}_2{}^a$	$\tilde{E}_3{}^a$	$2\langle 0 \mid V_0 \mid 1 \rangle^b$
0	0	0	1	0			
1	0	0	1	0	−0.0086	0.0001	0.19
1	1	0	0	0	−0.0151	0.0004	0.43
0	1	0	0	1	−0.0200	0.0009	0.37
0	1	0	0	2	−0.0212	0.0003	0.40
0	2	0	1	0	−0.0212	0.0003	0.39
2	1	0	0	0	−0.0248	0.0002	0.47
2	1	1	0	0	−0.0248	0.0002	0.47
2	0	1	1	0	−0.0248	0.0001	0.47

D. $(\sigma_u)^2$ Intrashell $^1\Sigma_g^+$ pair, f_{22} exponential parameter $= 1.1$

Basis function

p	q	r	s	m	$E_2{}^a$	$E_3{}^a$	$2\langle 0 \mid V_0 \mid 1 \rangle^b$
0	0	0	0	0			
0	0	0	0	1	0.0121	−0.0056	−0.01
0	1	0	1	0	−0.0120	−0.0034	0.60
0	1	0	1	1	−0.0789	0.0073	0.78
1	0	0	0	0	−0.0804	0.0093	0.78
0	0	0	2	0	−0.0824	0.0113	0.76
1	0	0	2	0	−0.0676	−0.5488	0.83
1	2	0	0	0	−0.1345	−0.0835	0.80
0	1	0	3	0	−0.1353	−0.1106	0.87
2	0	0	0	0	−0.1403	−0.0040	0.87
1	1	0	1	0	−0.1411	−0.0040	0.90

a Energies considering the pair in absence of other electrons, in atomic units.

b Matrix element of zero-order potential energy between zero-order and first-order (orthogonalized to zero-order) wavefunctions.

The Eqs. (35) and (36) are derivable by demanding that

$$E_v = \langle x \mid \tilde{\mathbf{H}}_0 - \tilde{E}^{(0)} \mid x \rangle + 2 \langle x \mid \tilde{\mathbf{H}}_1 - \tilde{E}_1^{(0)} \mid \Phi^{(0)} \rangle \quad (40)$$

be stationary with respect to arbitrary variations in x (the zero-order function $\tilde{\Phi}^{(0)}$ being fixed), and (39) results when x is taken in linear variational form. (The tilde distinguishes quantities for the two-electron problem.) For the ground state or lowest state of some symmetry, it may be shown[23,25] that the true second-order energy is a minimum with respect to variations in x, so addition of basis functions can only decrease E_v, which becomes equal to the second-order energy for the two-electron problem for a large enough basis set. For an excited state, we get a minimum principle for E_v when the contribution of other unperturbed states is being calculated exactly, that is, when the basis set is sufficiently flexible to represent these.[25]

The excited pair function u_{34} presents special problems. A large basis set was used and important terms selected, the same ones being used for $R = 0.7$ and $1.0a$. However, the lowest eigenvalue of $\mathbf{M}$ never gets very small so the full $\mathbf{M}^{-1}$ was used for these calculations. Orthogonality to the zero-order function was assured by orthogonalizing all basis functions to it. Since there are many unperturbed functions of the proper symmetry with energy lower than u_{34}^0, addition of basis functions does not necessarily decrease E_v. For $R = 0.7a_0$, there are in fact an infinite number of such states because the energy of this unperturbed state lies above the first ionization potential of the unperturbed two-electron system. The state is in the continuum and represents an autoionizing metastable state of He$_2^{2+}$. Variational calculations on such a state are possible[26] if the trial function used is incapable of representing the lower states or made orthogonal to them. The latter can be done by one-electron orthogonalizing it[27] to the lowest unperturbed orbital (1σ) since the lower-lying states are of the form $\mathcal{B}\{1\sigma n\sigma\}$ or $\mathcal{B}\{1\sigma k\sigma\}$ (bound or continuum states). In the He$_2$ calculation, putting the pair function into the first-order wavefunction [Eqs. (25) and (26)], does just this, because the antisymmetrization cancels off contributions to f_{22} of $\phi_{1\alpha}$ and $\phi_{1\beta}$. This comes out in the contribution of three and four-electron integrals to the second-order energy. (Pauli principle contraints of course are also present for the other pair functions, but are less important.) Imposing the one-electron orthogonality as a constraint in the solution of (35) would no longer give a true two-electron problem.[28]

[25] O. Sinanoğlu, Phys. Rev. **122**, 491 (1961); W. H. Miller, J. Chem. Phys. **44**, 2198 (1966).

[26] E. Høloien and J. Mitdal, J. Chem. Phys. **45**, 2209 (1966); H. S. Taylor and J. K. Williams, *ibid.* **42**, 4063 (1965).

[27] If a pair function is "strongly orthogonal" or "one-electron orthogonal" to an orbital, it is orthogonal to any two-particle configuration which includes that orbital. cf. O. Sinanoğlu, Proc. Roy. Soc. (London) **A260**, 379 (1961); W. Kutzelnigg, J. Chem. Phys. **40**, 3640 (1964).

[28] Byron and Joachain (Ref. 15) do this in their perturbation theory calculation for He starting from the Hartree–Fock.

Values of $\tilde{E}_2$ calculated for each pair function with increasing basis sets at $R = 1.0a_0$ are given in Table II. In addition, the third-order energies for the "free pairs," given by

$$\tilde{E}_3 = \langle x \mid \tilde{\mathbf{H}}_1 - \tilde{E}_1 \mid x \rangle + \tilde{E}_2 (\langle x \mid \tilde{\Phi}^{(0)} \rangle + \langle \tilde{\Phi}^{(0)} \mid x \rangle) \quad (41)$$

are listed. Here, $\tilde{E}_2 = E_v$ and $\tilde{\Phi}^{(0)}$ is the zero-order pair function. By following changes in $\tilde{E}_2$ and $\tilde{E}_3$ with addition of basis functions, we judge convergence. A table like Table II is not really appropriate for the last pair, since orthogonality (three-electron) corrections are extremely important. Thus, at $R = 1.0a_0$ we obtain -0.079 and -0.140 a.u. for $\tilde{E}_2$ using 5 and 14 functions, respectively, but the total contribution of this pair to the second-order energy of He$_2$ is -0.171 and -0.172 for the two cases.

The limiting values of $\tilde{E}_2$ and $\tilde{E}_3$ are of course not known, but another criterion is available, in the form of a condition that the true first-order wavefunction must satisfy. This condition, a consequence of the virial theorem, is relevant whenever the perturbation is a pure electrostatic potential energy term. It is analogous to a condition[29] for the atomic calculations, but is more complicated in form, because the virial theorem for a molecule[30] reads

$$\langle V \rangle = 2E + \sum_i (R_i \partial E / \partial R_i), \quad (42)$$

where the brackets indicate expectation value and the R_i are the internuclear distances needed to specify the molecular configuration (the Born–Oppenheimer separation is used). We are assuming $\mathbf{H} = \mathbf{H}_0 + \lambda \mathbf{H}_1$ with $\mathbf{H}_1$ an electrostatic potential-energy operator, and $\mathbf{H}_0 = \mathbf{T} + V_0$, where $\mathbf{T}$ is the kinetic-energy operator and V_0 the potential-energy operator in the unperturbed Hamiltonian. Equation (42) must hold all orders in the dummy perturbation parameter λ, with

$$\langle V \rangle = \frac{\langle \Phi^{(0)} + \lambda \Phi^{(1)} + \cdots \mid V_0 + \lambda V_1 \mid \Phi^{(0)} + \lambda \Phi^{(1)} + \cdots \rangle}{\langle \Phi^{(0)} + \lambda \Phi^{(1)} + \cdots \mid \Phi^{(0)} + \lambda \Phi^{(1)} + \cdots \rangle}$$

$$(43)$$

and $E = E^{(0)} + \lambda E^{(1)} + \cdots$. The zero-order equation

$$\langle \Phi^{(0)} \mid V_0 \mid \Phi^{(0)} \rangle = 2E^{(0)} + \sum_i (R_i \partial E^{(0)} / \partial R_i)$$

will be satisfied because $\Phi^{(0)}$ is an eigenfunction of $\mathbf{H}_0$. The first-order terms (taking $\langle \Phi^{(1)} \mid \Phi^{(0)} \rangle = 0$) are

$$\langle \Phi^{(1)} \mid V_0 \mid \Phi^{(0)} \rangle + \langle \Phi^{(0)} \mid V_0 \mid \Phi^{(1)} \rangle + \langle \Phi^{(0)} \mid V_1 \mid \Phi^{(0)} \rangle$$
$$= 2E^{(1)} + \sum_i R_i \partial E^{(1)} / \partial R_i \quad (44)$$

and the middle term on the left side is just $E^{(1)}$. For a diatomic, we have then

$$\langle \Phi^{(1)} \mid V_0 \mid \Phi^{(0)} \rangle + \langle \Phi^{(0)} \mid V_0 \mid \Phi^{(1)} \rangle = E^{(1)} + R \partial E^{(1)} / \partial R,$$

$$(45)$$

[29] R. E. Knight and C. W. Scherr, Rev. Mod. Phys. **35**, 431 (1963).

[30] Reference 4, Sec. 2.4.

with R the internuclear distance. A relation of this form holds for the many-particle wavefunction as well as for each pair function.

The right-hand side of (45) was estimated to a few percent for the various pairs from graphs of $E^{(1)}$ vs R. For the ground state, it is 0.66 a.u./a_0, for the intershell singlet and triplet, 1.38 and 0.47, for the excited intrashell pair, 1.08. The left-hand side is given for various functions in Table II, showing convergence to the proper value, except for the last pair.

IV. SECOND-ORDER ENERGY

In constructing $\Phi^{(1)}$, we will constrain each u_{ij} to be orthogonal to the corresponding $u_{ij}{}^0$. For a mixed pair, this means keeping ${}^3f_{ij}$ orthogonal to $\mathfrak{B}_{ij}\{\phi_i(i)\phi_j(j)\}$ and ${}^1f_{ij}$ orthogonal to $2^{-1/2}[\phi_i(i)\phi_j(j)+\phi_j(i)\phi_i(j)]$. Then $\Phi^{(0)}$ and $\Phi^{(1)}$ are orthogonal, and the second-order energy is given by

$$E^{(2)} = \langle \Phi^{(0)} \mid \mathbf{H}_1 - E_1 \mid \Phi^{(1)} \rangle$$

$$= \langle 2^{-1/2}X_1 \mid \mathbf{H}_1 \mid \sum_P (-1)^{\delta P}$$

$$\times P\{\lambda_1(1)\lambda_2(2)\cdots\lambda_N(N)\}\rangle. \quad (46)$$

The turn-over rule has been used in the second line. Explicitly, $E^{(2)}$ becomes

$$E^{(2)} = (1/\sqrt{2}) \sum_{i<j} \sum_{m<n} \langle \lambda_1(1)\cdots\lambda_N(N)$$

$$\times [u_{mn}(m, n)/\lambda_m(m)\lambda_n(n)] \mid g_{ij} \mid$$

$$\times \sum_P (-1)^{\delta P}P\{\lambda_1(1)\lambda_2(2)\cdots\lambda_N(N)\}\rangle.$$

There are three kinds of terms, depending on whether both i and j match m and n, one of i and j matches one of m and n, or neither i nor j matches m nor n. We write $E^{(2)} = E_\mathrm{I}{}^{(2)} + E_\mathrm{II}{}^{(2)} + E_\mathrm{III}{}^{(2)}$.

In the first case, we get

$$E_\mathrm{I}{}^{(2)} = \sum_{i<j} \langle u_{ij}(i,j) \mid g_{ij} \mid \mathfrak{B}_{ij}[\lambda_i(i)\lambda_j(j)]\rangle \quad (47)$$

which is a sum of two-electron terms. These are, in fact, just the quantities $\tilde{E}_2$ associated with the individual pair equations (cf. preceding section). For a mixed pair, the contribution is the average of the singlet and triplet results. The remaining terms in $E^{(2)}$ reflect the effects of orthogonality and one-electron corrections to the zero-order functions. If our zero-order function were the Hartree–Fock, and if the orthogonality to other orbitals were taken as a constraint on the pair functions in their calculation, there would be no such terms here.

The second case, where either m or n matches either i or j, leads to three-electron integrals. The contribution to the second-order energy may be written as

$$E_\mathrm{II}{}^{(2)} = \sqrt{2} \sum_{i<j} \sum_{n \neq i,j} \langle D_{ijn}(123) \mid g_{23} \mid u_{ij}(3,1)\lambda_n(2)\rangle,$$

$$(48)$$

where we have abbreviated

$$D_{ijn}(123) = \sum_P (-1)^{\delta P}P\{\lambda_i(1)\lambda_j(2)\lambda_n(3)\} \quad (49)$$

the sum going over the permutations of three particles. Finally, the four-electron terms here break down into products of two-electron terms.[31] Their expression may be put into the form

$$E_\mathrm{III}{}^{(2)} = 2 \sum_{i<j} \sum_{m<n} [\langle \mathfrak{B}_{12}[\lambda_i(1)\lambda_m(2)] \mid \langle \lambda_n(3)\lambda_j(4) \mid + \langle \mathfrak{B}_{12}[\lambda_m(1)\lambda_j(2)] \mid \langle \lambda_n(3)\lambda_i(4) \mid$$

$$+ \langle \mathfrak{B}_{12}[\lambda_j(1)\lambda_n(2)] \mid \langle \lambda_m(3)\lambda_i(4) \mid + \langle \mathfrak{B}_{12}[\lambda_n(1)\lambda_i(2)] \mid \langle \lambda_m(3)\lambda_j(4) \mid$$

$$+ \langle \mathfrak{B}_{12}[\lambda_i(1)\lambda_j(2)] \mid \langle \lambda_m(3)\lambda_n(4) \mid][g_{12} \mid \lambda_m(1)\lambda_n(2)\rangle \mid u_{ij}(3,4)\rangle], \quad (50)$$

where we have used the orthogonality of u_{ij} to $\mathfrak{B}(\lambda_i\lambda_j)$. In these sums, neither m nor n may equal i nor j.

The terms due to the Pauli principle (exclusion effects) may be brought into evidence by strongly orthogonalizing[27] each u_{ij} to spin–orbitals other than λ_i and λ_j. This is done by putting

$$u_{ij}(1,2) \to u_{ij}(1,2) - \sum_{n \neq i,j} [\lambda_n(1)\langle \lambda_n(3) \mid u_{ij}(3,2)\rangle + \lambda_n(2)\langle \lambda_n(3) \mid u_{ij}(1,3)\rangle]$$

$$+ \frac{1}{4} \sum_{m,n \neq i,j} [\lambda_m(1)\lambda_n(2) - \lambda_n(1)\lambda_m(2)]\langle \lambda_m(3)\lambda_n(4) - \lambda_n(3)\lambda_m(4) \mid u_{ij}(3,4)\rangle. \quad (51)$$

Inserting this into $E_\mathrm{I}{}^{(2)}$ [Eq. (47)], we pick up the last term in (50) and one third of the terms in (48). The remainder of the terms in $E_\mathrm{II}{}^{(2)}$ and $E_\mathrm{III}{}^{(2)}$ vanish when u_{ij} is strongly orthogonal to λ_i and λ_j (Hartree–Fock case).

The next step is the reduction of $E_\mathrm{II}{}^{(2)}$ and $E_\mathrm{III}{}^{(2)}$ to integrals involving spatial functions only. For $E_\mathrm{II}{}^{(2)}$, 16 three-electron integrals appear. Defining

$$\mathfrak{g}_i = \int d\tau_1 d\tau_2 d\tau_3 f(1,2)\phi_k(3)g_{23}\phi_l(1)\phi_m(2)\phi_n(3), \quad (52)$$

where the specification of f and the values of k, l, m, and n are given in Table III, we find

$$E_\mathrm{II}{}^{(2)} = 4\mathfrak{g}_1 - 2\mathfrak{g}_2 - 2\mathfrak{g}_3 + 3\sqrt{2}(\mathfrak{g}_4 - \mathfrak{g}_5) - \sqrt{2}(2\mathfrak{g}_6 - \mathfrak{g}_7 - \mathfrak{g}_8)$$

$$+ 3\sqrt{2}(\mathfrak{g}_9 - \mathfrak{g}_{10}) + 4\mathfrak{g}_{12} - 2\mathfrak{g}_{11} - 2\mathfrak{g}_{13} - \sqrt{2}(2\mathfrak{g}_{16} - \mathfrak{g}_{14} - \mathfrak{g}_{15}).$$

$$(53)$$

Some of the $\mathfrak{g}_i$ are zero in the present case because of the

[31] This is equivalent to the remark of Layzer et al. (Ref. 2c) that the contribution of double virtual excitations can be obtained from two-electron quantities.

g–u symmetry. For $E_{\text{III}}^{(2)}$, this and orthogonality constraints make most of the terms zero, and we are left with

$$E_{\text{III}}^{(2)} = \int d\tau_1 d\tau_2 \phi_2(1)\phi_2(2) g_{12}\phi_1(1)\phi_1(2)$$

$$\times \left[\int\int d\tau_3 d\tau_4 [\phi_1(1)\phi_1(2)f_2(1,2)]\right.$$

$$\left. + \int d\tau_1 d\tau_2 \phi_2(1)\phi_2(2)f_1(1,2) \right]. \quad (54)$$

The three-electron integrals were evaluated numerically by essentially the methods used for two-electron

TABLE III. Definitions of $\mathcal{g}_i$:

$$\mathcal{g}_i = \int d\tau_1 d\tau_2 d\tau_3 f(1,2)\phi_k(3) g_{23}\phi_l(1)\phi_m(2)\phi_n(3)$$

with f, k, l, m, n given for each i.

i	f	k	l	m	n
1	f_{11}	2	1	1	2
2	f_{11}	2	2	1	1
3	f_{11}	2	1	2	1
4	$^3f_{12}$	1	1	2	1
5	$^3f_{12}$	1	2	1	1
6	$^1f_{12}$	1	1	1	2
7	$^1f_{12}$	1	1	2	1
8	$^1f_{12}$	1	2	1	1
9	$^3f_{12}$	2	1	2	2
10	$^3f_{12}$	2	2	1	2
11	f_{22}	1	2	1	2
12	f_{22}	1	2	2	1
13	f_{22}	1	1	2	2
14	$^1f_{12}$	2	1	2	2
15	$^1f_{12}$	2	2	1	2
16	$^1f_{12}$	2	2	2	1

integrals, mentioned in the previous section. After explicit integrations over the three angular coordinates crossed Gauss quadrature formulas are used for the remaining six dimensions. The evaluation of the integrals was performed on the IBM 1800 computer of the Department of Chemistry and Chemical Engineering. With a few thousand integration points the integrals are accurate to about 5%, judging from changes on increasing the number of points. This leads to an error of the order of a hundredth of an atomic unit in the second-order energy.

The error due to truncation of the basis sets used for the pair function, from a study of the $R=0.7$ results, is about the same order of magnitude. Thus, the second-

TABLE IV. Second-order energy by pairs and by 2-, 3-, and 4-electron contributions, bare nuclei.

Pair	$E^{(2)}_{\text{I}}$	$E^{(2)}_{\text{II}}$	$E^{(2)}_{\text{III}}$	Total
$R=0.7$				
$(\sigma_g)^2$	-0.1085	-0.024	-0.0093	-0.142
$^1\Sigma_u^+$	-0.1763	-0.069	0.0	-0.245
all $^3\Sigma_u^+$	-0.0987	-0.236	0.0	-0.335
$(\sigma_u)^2$	-0.1161	-0.092	0.0111	-0.197
Total	-0.4996	-0.421	0.0018	-0.919
$R=1.0$				
$(\sigma_g)^2$	-0.1053	0.010	-0.0220	-0.118
$^1\Sigma_u^+$	-0.1561	-0.043	0.0	-0.199
all $^3\Sigma_u^+$	-0.0744	-0.180	0.0	-0.254
$(\sigma_u)^2$	-0.1411	-0.092	0.0240	-0.209
Total	-0.4709	-0.305	0.0020	-0.780

order energy is probably correct to a few percent, which is sufficient for our present purposes. The approximate second-order energy calculated here is necessarily an upper bound to the true value because we are dealing with the ground state of He₂. Since it may be broken down into a sum of pair contributions, each pair contribution would be lowered by use of more variational parameters in the pair function—including, of course, the three- and four-electron terms with the pair contribution. In Table IV, we give the contributions of the various pairs to the second-order energy, and also show the breakdown into two-, three-, and four-electron terms ($E_{\text{I}}^{(2)}$, $E_{\text{II}}^{(2)}$, $E_{\text{III}}^{(2)}$) at the two internuclear distances.

An elegant method for evaluation of the 3-electron contributions to $E^{(2)}$, at least for atoms, is given by Chisolm and Dalgarno.[2b] It involves recognition that these represent virtual single-electron transitions and can be expressed in terms of functions related to the Hartree–Fock functions. We have not attempted this here.

Table V gives the zero-, first-, and second-order energy for the bare-nucleus perturbation theory at the

TABLE V. Bare-nucleus results (energies in atomic units).

R (a_0)	0.7	1.0
$E^{(0)}$	-15.171	-14.161
$E^{(0)}+E^{(1)}$	-8.652	-8.027
$E^{(0)}+E^{(1)}+E^{(2)}$	-9.571	-8.807
E_{BCF}[a]	-9.690[b]	-8.793
E_{CI}[c]	-9.785[b]	-8.858

[a] Matsumoto, Bender, and Davidson, Ref. 22.
[b] Interpolated from data of Ref. 22.
[c] Fifty configurations of natural orbitals, Ref. 22.

two internuclear distances considered. In addition, we have given the energy from the SCF calculation (best single determinant) and the energy from a 50-configuration calculation using natural orbitals, both by Matsumoto, Bender, and Davidson.[22] They give results for $R=0.25$, 0.50, 0.75, and $1.00a_0$: the numbers cited for 0.70 were roughly interpolated by us.

Basis sets of increased size for the pair functions will necessarily lower $E^{(2)}$. We have estimated the size of such lowering as a few hundredths of an atomic unit. In addition, the third-order energy could be calculated from

$$E^{(3)} = \langle \Phi^{(1)} \mid \mathbf{H}_1 - E_1 \mid \Phi^{(1)} \rangle. \qquad (55)$$

(This assumes $\langle \Phi^{(1)} \mid \Phi^{(0)} \rangle = 0$.) The reduction of (55) leads to a very large number of two-electron and multi-electron integrals.[2a] It does not break down into a sum of pair contributions, although Byron and Joachain[15] have argued that the interpair terms were small for their calculation. We have not attempted to evaluate it here. The two-electron contributions to $E^{(3)}$ are of the form $\langle u_{ij} \mid g_{ij} - \widetilde{E}_{ij}^{(1)} \mid u_{ij} \rangle$, with $\widetilde{E}_{ij}^{(1)} = \langle u_{ij}^0 \mid g_{ij} \mid u_{ij}^0 \rangle$, i.e., the third-order energies of the individual pair. They are hundredths of an atomic unit in size, which may reflect the size of the full $E^{(3)}$. $E^{(3)}$ was positive for ground state two-electron calculations[12–14] but negative for the three-electron atom.[2a] It is possible that a better calculation of $E^{(2)}$ and a knowledge of $E^{(3)}$ could lead to a good energy for this calculation.

The results through $E^{(2)}$ are not good. With a zero-order Hamiltonian that ignores interelectronic interaction entirely, the energy series converges too slowly.

V. SCREENED-NUCLEUS PERTURBATION THEORY

The problem is that the outer electrons in the molecule see an effective total nuclear charge of less than 4 because of screening by the inner electrons. Putting them into orbitals corresponding to a charge of 4 is a bad place to start. There will also be screening of the σ_g electrons by the σ_u electrons to some extent, as well as interactions between electrons in the same shell, but the screening becomes more important for electrons in different shells.[20,32]

To choose a better $\mathbf{H}_0$, which is to incorporate some of the effect of interelectronic repulsion, we use the idea of screened nuclei, introduced in Sec. I. The effective charge, which enters $\mathbf{H}_0$, is chosen so that $E^{(0)}+E^{(1)}$, calculated with $\mathbf{H}_0$, is minimized and thus as close as possible to the true energy of He_2. For $R=1.0$, choosing this charge as 1.5 yields $E^{(0)} = -8.425$ a.u. and $E^{(1)} = -0.239$. $E^{(0)}+E^{(1)}$ has gone from -8.027 (bare nuclei) to -8.664, i.e., 5/6 the distance to the SCF, while the quantity $\mid E^{(1)}/E^{(0)} \mid$ (sometimes taken as a crude measure of convergence) has gone from 0.433 to 0.028.

[32] C. Scherr, F. C. Sanders, and R. E. Knight, in *Perturbation Theory and Its Applications in Quantum Mechanics*, C. H. Wilcox, Ed. (John Wiley & Sons, Inc., New York, 1966).

The calculations to follow were carried out at internuclear distances of 0.9, 1.0, and $1.1a_0$, with the effective charge for $\mathbf{H}_0$ taken as 1.5 for all three cases.

The zero-order problem, noninteracting electrons in the field of nuclei of charge 1.5, is not physical, but is of course as easily solved as the problem for integral charges. We now show that, for the first-order wavefunction, we can use the formalism of Sec. II, but that the pair functions do not correspond to the He_2^{++} system as in the bare-nucleus case.

For generality, we suppose that we choose

$$\mathbf{H}_0 = \sum_{i=1}^{N} (h_i^0 + f_i), \qquad (56)$$

where f_i is a function of the spatial coordinates of electron i. Then $\mathbf{H}_1$ may be rewritten as follows:

$$H_1 = \sum_{i<j} g_{ij} - \sum_{i=1}^{N} f_1$$
$$= \sum_{i<j} g_{ij} - (N-1)^{-1} \sum_{i<j} (f_i + f_j). \qquad (57)$$

We define the right member of (57) as $\sum_{i<j} h_{ij}$. Now if we put h_{ij} for g_{ij} and $h_i^0 + f_i$ for h_i^0 in all the equations of Secs. II and III, we may take over the entire bare-nucleus perturbation theory formalism. The perturbation h_{ij} may be thought of as a screened-interelectronic interaction.

In the present case, f_i contains the residual electron-nuclear attraction, corresponding to a nuclear charge of 0.5. Because of the $(N-1)^{-1}$ factor, our two-electron perturbation equations correspond to the states of a homonuclear diatomic with nuclear charge $3/2 + 1/6$. The perturbation is still Coulombic, so the criterion of Eq. (45) is still useful.

In Table VI we give the results obtained for the calculations on the first three pair functions at $R=1.0a_0$. The exponential parameter in each case was determined from experiments with small basis sets at $R=1.0$, and the same value (as well as the same final basis set) was used for the other two distances. From the plots of $\widetilde{E}^{(1)}$ vs R, we find the quantity $\widetilde{E}^{(1)} + R d\widetilde{E}^{(1)}/dR$ at $R=1.0$ to be 0.080 ± 0.001 for $(\sigma_g)^2$, 0.244 ± 0.002 for $^1\Sigma_u^+$, and -0.075 ± 0.002 for $^3\Sigma_u^+$. We believe the contributions of the first three pairs of $E^{(2)}$ have converged to ~ 0.0015 a.u. This is based on the convergence of $\widetilde{E}^{(2)}$ and $\widetilde{E}^{(3)}$ and also on the convergence of each pair contribution including three- and four-electron terms. The energy of the ground state of the homonuclear diatomic with nuclear charges of 10/6 and internuclear distance $0.9a_0$ can be calculated from Matcha's results[12a] for charges of 1 and internuclear distance 1.5, using the scaling procedure of Sec. III. We find -5.779 a.u.; our calculation gives -5.778 a.u.

For the $(\sigma_u)^2$ pair, we tried several different basis sets and exponential parameters at each value of R. $\widetilde{E}^{(2)}$ here may vary widely with addition of basis functions but the total contribution of the pair to $E^{(2)}$ will decrease to a

TABLE VI. Pair functions for $R = 1.0\ a_0$, screened nuclei.

Basis function							
p	q	r	s	m	$\tilde{E}^{(2)}$ [a]	$\tilde{E}^{(3)}$ [a]	$\langle 0 \mid V_0 \mid 1 \rangle$ [a]

A. Ground-state pair. $\bar{\alpha}=1.15$, $\tilde{E}^{(0)}=-5.62045$, $\tilde{E}^{(1)}=0.14435$ a.u.

p	q	r	s	m	$\tilde{E}^{(2)}$	$\tilde{E}^{(3)}$	$\langle 0 \mid V_0 \mid 1 \rangle$
0	0	0	0	0			
0	0	0	0	1	−4.99	0.43	18.41
0	0	0	2	0	−5.12	0.45	16.41
1	0	0	0	0	−5.82	0.57	7.69
0	1	0	1	0	−6.10	0.47	8.06
0	0	0	2	1	−6.15	0.46	8.02
2	0	0	0	0	−6.23	0.42	8.32
2	0	0	0	1	−6.36	0.48	8.16
1	0	1	0	0	−6.37	0.47	8.05
1	0	0	0	1	−6.37	0.47	8.04
1	0	0	2	0	−6.37	0.47	8.04
0	0	0	0	2	−6.52	0.61	8.14
3	0	0	0	0	−6.52	0.61	8.13
1	2	0	0	0	−6.54	0.62	8.05
0	4	0	0	0	−6.54	0.62	8.04
1	0	0	0	2	−6.56	0.63	8.00
1	0	1	0	1	−6.56	0.64	8.00
1	1	0	1	0	−6.56	0.64	8.00
1	1	1	1	0	−6.56	0.63	8.00
1	0	0	2	1	−6.56	0.64	8.00

B. Intershell triplet. $\bar{\alpha}=1.03$, $\tilde{E}^{(0)}=-4.21235$, $\tilde{E}^{(1)}=-0.19648$ a.u.

p	q	r	s	m	$\tilde{E}^{(2)}$	$\tilde{E}^{(3)}$	$\langle 0 \mid V_0 \mid 1 \rangle$
0	0	0	1	0			
0	1	0	0	1	−0.14	0.006	3.45
1	0	0	1	0	−0.18	0.009	2.70
1	1	0	0	0	−1.06	0.024	−6.74
0	2	0	1	0	−1.11	0.009	−7.17
1	0	0	1	1	−1.13	0.009	−7.45
1	1	0	0	1	−1.16	0.023	−6.15
2	0	0	1	0	−1.31	0.025	−6.85
0	3	0	0	0	−1.32	0.020	−6.97
0	3	1	0	0	−1.32	0.020	−6.96
0	1	0	0	2	−1.35	0.015	−7.28
1	1	1	0	0	−1.40	0.021	−6.94
1	1	0	2	0	−1.42	0.024	−7.06
2	1	0	0	0	−1.44	0.036	−7.74
3	0	0	1	0	−1.44	0.036	−7.73
2	1	1	0	0	−1.46	0.036	−7.81
0	1	0	2	1	−1.46	0.036	−7.80
1	0	0	1	2	−1.47	0.037	−7.77
2	0	1	1	0	−1.47	0.036	−7.81
1	2	1	1	0	−1.47	0.035	−7.85

C. Intershell singlet. $\bar{\alpha}=0.71$, $\tilde{E}^{(0)}=-4.21235$, $\tilde{E}^{(1)}=0.16910$ a.u.

p	q	r	s	m	$\tilde{E}^{(2)}$	$\tilde{E}^{(3)}$	$\langle 0 \mid V_0 \mid 1 \rangle$
0	0	0	1	0			
0	1	0	0	1	−3.93	0.08	18.13
1	0	0	1	0	−5.57	0.32	13.68
1	1	0	0	0	−5.73	0.18	17.69
0	2	0	1	0	−5.98	0.18	17.02
1	0	0	1	1	−6.59	0.29	22.64
1	1	0	0	1	−6.59	0.32	22.65
2	0	0	1	0	−7.80	0.17	20.60
0	1	0	0	2	−7.86	0.31	20.32
1	1	1	0	0	−8.14	0.10	22.56
1	1	0	2	0	−8.21	0.082	22.80
2	1	0	0	0	−8.26	0.039	23.09
3	0	0	1	0	−8.31	0.038	23.06
2	1	1	0	0	−8.36	−0.094	23.53
0	1	0	2	1	−8.36	−0.097	23.61
1	0	0	1	2	−8.69	0.035	23.83
2	0	1	1	0	−8.76	−0.064	24.20
1	2	1	1	0	−8.83	−0.092	24.01
2	0	0	1	1	−8.83	−0.091	23.98
2	1	0	0	1	−8.84	−0.049	24.30
2	1	2	0	0	−8.93	−0.065	24.37
1	1	0	0	2	−8.93	−0.060	24.43

[a] In units of 10^{-2} a.u. $= 0.2721$ eV. $\bar{\alpha}$ is the exponential parameter.

TABLE VII. Screened nuclei: second-order energy by pairs and by 2-, 3-, and 4-electron contributions (energies in atomic units).

Pair	$E_{\mathrm{I}}^{(2)}$	$E_{\mathrm{II}}^{(2)}$	$E_{\mathrm{III}}^{(2)}$	Total
$R=0.9$				
σ_g^2	−0.06278	0.0274	−0.0085	−0.0439
$^1\Sigma_u^+$	−0.09518	0.0355	···	−0.0597
$^3\Sigma_u^+$	−0.04049	−0.0182	···	−0.0587
σ_u^2	−0.06879	0.0233	0.0121	−0.0334
Total	−0.2672	0.0680	0.0036	−0.1957
$R=1.0$				
σ_g^2	−0.06565	0.0319	−0.0119	−0.0456
$^1\Sigma_u^+$	−0.08932	0.0379	···	−0.0514
$^3\Sigma_u^+$	−0.04314	−0.0171	···	−0.0602
σ_u^2	−0.07111	0.0212	0.0149	−0.0350
Total	−0.2692	0.0739	0.0030	−0.1922
$R=1.1$				
σ_g^2	−0.06839	0.0370	−0.0155	−0.0469
$^1\Sigma_u^+$	−0.08360	0.0387	···	−0.0449
$^3\Sigma_u^+$	−0.04611	−0.0170	···	−0.0631
σ_u^2	−0.05006	0.0065	0.0173	−0.0262
Total	−0.2482	0.0652	0.0018	−0.1812

limit. However, if $\tilde{E}^{(2)}$ becomes too large, the three-electron contributions must also become large, and the error in their calculation will become significant. From our experiments, we place an error of $\sim$0.005 a.u. on the contribution of this pair to $E^{(2)}$. The second-order energy is given in Table VII for the three values of R, broken down by pairs and by type of contribution.

If the perturbation series converges quickly enough, the third-order energy, which is too complicated for us to calculate, may be neglected. We believe this to be the case here, i.e., $E^{(3)}$ is probably not larger than the error in $E^{(2)}$ of $\sim$0.01 a.u. To encourage this belief, we have the fact that $\tilde{E}^{(3)}$ is less than 0.01 for the $(\sigma_g)^2$ pair and less than 0.001 for $^1\Sigma_u^+$ and $^3\Sigma_u^+$. Note that while more accurate calculation of $E^{(2)}$ would necessarily lower our total energy, $E^{(3)}$ may be positive or negative.

VI. RESULTS AND DISCUSSION

The results of our screened-nucleus perturbation theory are displayed in Table VIII. We believe the energy to be good to several hundredths of an atomic unit in each case. While experiments on He–He scattering can in principle give the energy for this system as a function of internuclear distance, we compare our results with calculations performed by other (variational) methods. Among other workers, Barnett[33] has used two open-shell configurations with up to 16

[33] G. P. Barnett, Can. J. Phys. **45**, 137 (1967).

TABLE VIII. Summary of screened-nuclei results for electronic energy and comparisons (energies in atomic units).

$R(a_0)$	0.9	1.0	1.1
$E^{(0)}$	-8.59114	-8.42470	-8.27440
$E^{(0)}+E^{(1)}$	-8.88435	-8.66361	-8.47674
$E^{(0)}+E^{(1)}+E^{(2)}$	-9.080	-8.856	-8.655
$E(\text{SCF})$[a]	-9.03[d]	-8.793	$\cdots$
$E(2 \text{ config.})$[b]	$\cdots$	-8.807	$\cdots$
$E(64 \text{ CI})$[c]	-9.07[d]	-8.84[d]	-8.64[d]
$E(\text{NO-CI})$[a]	-9.08[d]	-8.858	$\cdots$

[a] Reference 35.
[b] Reference 33.
[c] Reference 34.
[d] Interpolated to $\sim$0.01 a.u.

nonlinear parameters, Phillipson[34] got slightly better results from configuration interaction (64 configurations), and the best results are those of Matsumoto, Bender, and Davidson,[35] who employed 50 configurations of natural orbitals (NO–CI). They also give one-configuration (SCF) results. A many-electron perturbation theory calculation for large internuclear distance exists, by Kestner and Sinanoğlu.[36]

Our results are quite close to the NO–CI work of Matsumoto *et al.* However, these authors estimate that the true energies are still 0.02 a.u. below their results. It must also be noted that perturbation results are not necessarily an upper bound to the true energies (unless $E^{(3)}$ and higher terms in the energy may be neglected).

We believe that the present work shows that first-order perturbation theory calculations for molecular systems with several electrons are practicable, and that accurate results may be obtained by calculation of the energy through $E^{(2)}$. We plan to do further calculations on other systems. However, there are several unsatisfactory features, at least some of which can be avoided.

As mentioned above, problems arise with the doubly-excited pairs because of the large number of lower-lying two-electron zero-order states, especially if they are embedded in the continuum. In both the bare-nucleus and screened-nucleus calculations, though, a small change of internuclear distance takes $(\sigma_u)^2$ out of the continuum. One expects that, in many cases, a slight change of the zero-order charge in a screened-nucleus calculation can do the same, without appreciably affecting the convergence of the energy. Similarly, the number of lower-lying discrete two-electron zero-order states can be reduced by such a change.

The convergence of the pair functions for the singly-excited pairs is slow. As for the corresponding cases in H_2 [20] we believe the situation can be improved by modifying the basis functions (38). Use of open-shell functions with several nonlinear parameters can replace extensive configuration interaction in variational calculations[38,37] and should do the same here.

Finally, the convergence of the perturbation series may be further improved if one chooses a better $\mathbf{H}_0$. Chemical accuracy ($\sim$1 kcal) may be obtainable here without calculation of $E^{(3)}$ for a sufficiently good choice. It seems unlikely, in any case, that screened nuclei will be adequate if one goes to a system with many more than four electrons. We are completely free to use physical intuition or other information to construct non-Coulombic potentials for which $E^{(0)}+E^{(1)}$ is smaller, so that the zero-order function is closer to the exact wave-function, while still maintaining $\mathbf{H}_0$ local and one-electron. For instance, since electrons in the inner orbital should feel a larger nuclear charge than the outer electrons, a "Coulomb" potential with effective nuclear charge depending on distance would take care of this. The ideal one-electron choice, the SCF, cannot be used, as discussed in Sec. I, but approximations to it (possibly with simulation of the exchange by a local potential) may be possible.

[34] P. E. Phillipson, Phys. Rev. **125**, 1981 (1962).
[35] G. H. Matsumoto, C. F. Bender, and E. R. Davidson, J. Chem. Phys. **46**, 402 (1967).
[36] N. R. Kestner and O. Sinanoğlu, J. Chem. Phys. **45**, 194 (1966).

[37] H. H. Michels, J. Chem. Phys. **44**, 3834 (1966).