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First-Order Perturbation Corrections to the Hartree-Fock Approximation for Helium*

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Variational perturbation theory has been used to compute the first-order wave function for the ground state of the helium atom, in a scheme where the Hartree-Fock function is treated as the zeroth-order approximation. The first-order function was approximated by a Hylleraas-like expansion, explicitly containing r_{12}. We obtain a total energy through third order of -2.90262 a.u., as compared with the nonrelativistic eigenvalue of -2.90372. The first-order corrections to expectation values of a selection of one- and two-electron operators have been computed. The calculations have also been done for the isoelectronic ions, H^-, Li^+, and Be^{++}.

INTRODUCTION

IT is well known that the Hartree-Fock approximation neglects the details of the interelectronic repulsions, treating them in only an average fashion. The resulting error, which has come to be known as the "correlation error," can for many purposes be significant. A considerable body of literature has come into existence dealing with just this problem in a variety of ways.[1] Almost invariably, the approach has been to approximate the many-electron eigenfunction by a variational wave function, which explicitly accounts, to some extent at least, for the electron correlation. The most successful of these approaches has given the ground-state energy of the helium atom to well within the experimental uncertainties.[2]

In this paper, we follow a somewhat different approach, which has not yet received much computational attention, although the formalism has been discussed by several authors.[3–6] The total Hamiltonian is separated into two parts: one part consisting of the sum of the Fock operators, for which the Hartree-Fock orbitals are eigenfunctions, and a second part containing everything that is left over, which is treated as a perturbation. The N-electron Hartree-Fock function then becomes the first term (zeroth order) in a perturbation expansion of the exact wave function, all the correlation effects being thrown into the higher order corrections.

We report here variational calculations of the first-order function for the ground state of the helium atom (and some isoelectronic ions), based on the variational

principle for the second-order energy.[7] In particular, to obtain definitive numerical results, the first-order function has been approximated by a Hylleraas-like expansion explicitly involving nonnegative powers of r_{12}. The primary purpose of this investigation is to isolate, for a simple system, how much of the correlation effects are contained in the first-order correction, with the intention of assessing the possibilities of the scheme for more complex systems.

There is another more conventional way of applying the variation-perturbation procedure to atomic systems, which deserves mention at this point.[8] This scheme, which we will refer to as the "hydrogenic" perturbation approach, takes the sum of the bare-nucleus (hydrogen-like) Hamiltonians as the zeroth-order Hamiltonian and treats the entire interelectronic repulsion as the perturbation. The perturbation expansion of the energy and all expectation values becomes a descending power series in the nuclear charge, Z. There has recently been a renewed interest in this approach,[9–12] and we will be making comparisons between it and the present "Hartree-Fock perturbation" scheme.

GENERAL THEORY

The nonrelativistic Hamiltonian for the helium atom is given by

$$\mathcal{K} = h(1) + h(2) + 1/r_{12}, \tag{1}$$

where $h(i)$ is the "bare nucleus" Hamiltonian,[13]

$$h(i) = -\tfrac{1}{2}\Delta_i - Z/r_i. \tag{2}$$

For the ground state, the Hartree-Fock wave function is a simple orbital product function,

$$\Psi_0 = \varphi(1)\varphi(2) \tag{3}$$

[1] Rather than attempt to cite all the relevant literature, the reader is referred to several reviews on the subject. See, e.g., P. O. Lowdin, *Advances in Chemical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. 2; J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. 2.
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[13] Atomic units are used throughout this paper. Distance is in units of the Bohr radius, and energy in units of $2R_M$, where R_M is the reduced mass Rydberg.

where we have suppressed the spin part of the function, and the orbitals are eigenfunctions of the Fock operator;

$$F(i)\varphi(i) = \eta\varphi(i), \qquad (4a)$$

$$F(i) = h(i) + J_\varphi(i), \qquad (4b)$$

$$J_\varphi(i) = \int dV_j(|\varphi(j)|^2/r_{ij}). \qquad (4c)$$

J_φ is the usual Coulomb operator of self-consistent field theory and η the orbital energy.

The Hamiltonian (1) can be rewritten in the following fashion:

$$\mathfrak{K} = \mathfrak{K}_0 + V \qquad (5)$$

with

$$\mathfrak{K}_0 = F(1) + F(2); \qquad (6a)$$

$$V = 1/r_{12} - J_\varphi(1) - J_\varphi(2). \qquad (6b)$$

Now, the Hartree-Fock function is an eigenfunction of $\mathfrak{K}_0$, which we treat as a zeroth-order Hamiltonian,

$$\mathfrak{K}_0\psi_0 = 2\eta\psi_0, \qquad (7)$$

and V, the "fluctuation potential", becomes a perturbation. The exact wave function and energy are given by the perturbation series,

$$\Psi = \psi_0 + \psi_1 + \psi_2 + \cdots \qquad (8a)$$

$$E = \epsilon_0 + \epsilon_1 + \epsilon_2 + \epsilon_3 + \cdots, \qquad (8b)$$

where the ψ_i's are solutions of the equations

$$(\mathfrak{K}_0 - \epsilon_0)\psi_1 = \epsilon_1\psi_0 - V\psi_0, \qquad (9a)$$

$$(\mathfrak{K}_0 - \epsilon_0)\psi_2 = \epsilon_2\psi_0 + \epsilon_1\psi_1 - V\psi_1, \qquad (9b)$$

$$\vdots$$

and the energies are given by the standard expressions,

$$\epsilon_0 = 2\eta, \qquad (10a)$$

$$\epsilon_1 = \langle\psi_0|V|\psi_0\rangle = -\langle\varphi|J_\varphi|\varphi\rangle, \qquad (10b)$$

$$\epsilon_2 = \langle\psi_0|V|\psi_1\rangle, \qquad (10c)$$

$$\epsilon_3 = \langle\psi_1|V - \epsilon_1|\psi_1\rangle. \qquad (10d)$$

Also, the expectation of any operator f, through first order, is given by

$$\langle\psi|f|\psi\rangle_1 = \langle\psi_0|f|\psi_0\rangle + 2\langle\psi_0|f|\psi_1\rangle. \qquad (11)$$

The Hartree-Fock total energy, in terms of the perturbation energies, is

$$E_{HF} = \epsilon_0 + \epsilon_1 = 2\eta - \langle\varphi|J_\varphi|\varphi\rangle. \qquad (12)$$

It should be noted, in Eqs. (10) and (11), that we have taken Ψ_1 orthogonal to Ψ_0, which can be done without loss of generality and insures the normalization of the total wave function through first order.

As is well known,[7] these perturbation equations can be obtained by a variational principle; namely, making the following integral an extremum:

$$I = \langle\psi_1|(\mathfrak{K}_0 - \epsilon_0)\psi_1 - 2(\epsilon_1 - V)\psi_0\rangle, \qquad (13)$$

with respect to an arbitrary variation of Ψ_1, leads to Eq. (9a). For the exact Ψ_1, (13) is just the second-order energy, while for an approximate function, it is an upper bound to ϵ_2. If, now, one approximates Ψ_1 by a linear combination of basis functions,

$$\Psi_1 = \sum_p c_p\phi_p, \qquad (14)$$

and applies this variational principle, the matrix analog of (9a) results,

$$(H_0 - \epsilon_0 S)c = \epsilon_1 s - v, \qquad (15)$$

where the matrix and vector elements are given by

$$(H_0)_{pq} = \langle\phi_p|\mathfrak{K}_0|\phi_q\rangle, \quad (S)_{pq} = \langle\phi_p|\phi_q\rangle, \qquad (16)$$
$$(s)_p = \langle\Psi_0|\phi_p\rangle, \qquad (v)_p = \langle\Psi_0|V|\phi_p\rangle.$$

For the present calculations, Ψ_1 was approximated by a Hylleraas-like expansion,

$$\Psi_1 = (8\pi)^{-1}\sum_{ij\mu} c_{ij\mu}\zeta^6 e^{-\rho_1 - \rho_2}(\rho_1{}^i\rho_2{}^j + \rho_1{}^j\rho_2{}^i)\rho_{12}{}^\mu,$$

$$\rho = \zeta r, \qquad (17)$$

where ζ is an additional variational parameter available for minimizing ϵ_2. For purposes of computing the matrix elements, analytic approximations for the Hartree-Fock orbitals were used, expanding them in the standard set of Slater-type orbitals (STO's);

$$\varphi = \sum_{n,a} a_{na}(2\alpha)^{n+\frac{1}{2}}(4\pi(2n)!)^{-1/2}r^{n-1}e^{-\alpha r}. \qquad (18)$$

All the matrix elements (16) can be reduced to the usual two-electron integrals of the conventional variational calculations. The reduction of matrix elements involving J_φ to these integrals is given in an Appendix.

The more conventional hydrogenic perturbation scheme is obtained by taking the first two terms of (1), the "bare nucleus" Hamiltonians, as the zeroth-order Hamiltonian and the entire electronic repulsion as the perturbation. The zeroth-order solution is an orbital product of hydrogenic functions, and the wave function and energy expansions become descending power series in Z, the energy series beginning with Z^2.

RESULTS AND DISCUSSION

The energies computed for helium with expansion lengths as high as 50 terms are shown in Table I. The notation E_3 refers to the total energy computed through third order, i.e.,

$$E_n = \sum_{i=0}^{n} \epsilon_i.$$

The second- and third-order energies appear to be reasonably well converged and probably represent the true values to at least four decimal places. It is, however,

TABLE I. Hartree-Fock perturbation energies (in a.u.) for the ground state of helium.

Maximum of $i+j+\mu$ in Eq. (17)	No. of terms in Ψ_1	e_2	e_3	E_3
2	7	-0.04763	0.00670	-2.90262
3	13	-0.04817	0.00722	-2.90263
4	22	-0.04832	0.00737	-2.90263
5	34	-0.04834	0.00740	-2.90262
6	50	-0.04835	0.00741	-2.90262

$$E_{H-F} = -2.86168$$
$$E_{exact} = -2.90372^a$$

a See Ref. 2.

somewhat discouraging that the total energy is no closer to the eigenvalue. The error is about 0.03 eV, which may well portend substantial energy errors if the scheme were applied to much larger systems, say 6 to 10 electrons.

Our numerical experience also indicates that no more than the number of figures given are really significant; there may even be an uncertainty of 1 or 2 in the last place. The reason is apparently the approximate nature of the zeroth-order (Hartree-Fock) functions, which, of course, are not known exactly. This is a limitation that will probably apply to any scheme which explicitly incorporates the Hartree-Fock solutions as a starting point. It is, perhaps, curious to note that the total energy through third order is quite insensitive to the accuracy with which ψ_1 is approximated, even though the individual e_2 and e_3 are not.

The expectation values of a selection of operators and their first-order corrections are shown in Table II. The first-order corrections were computed with the 50-term function; calculations with the smaller wave functions indicated good convergence for all the values given. The zeroth-order part, of course, is just the Hartree-Fock expectation value. It has been shown that the first-order correction to a Hartree-Fock expectation value of any one-electron operator should vanish identically,[6] and this is borne out by our direct calculations. This feature, in fact, provided a nice additional check on our numerical work. For one-electron operators, therefore, the Hartree-Fock results are unchanged, and

TABLE II. First-order corrections to the Hartree-Fock expectation values of some one- and two-electron operators.

f	$\langle 0|f|0\rangle$	$\langle 0|f|1\rangle$	$\langle f\rangle_1$	$\langle f\rangle_{exact}^a$
r_1^{-1}	1.6874	-0.0001	1.6872	1.6883
r_1	0.9273	0.0000	0.9272	0.9295
r_1^2	1.1849	0.0000	1.1849	1.1935
r_{12}^{-1}	1.0258	-0.0483	0.9291	0.9458
r_{12}	1.3622	0.0351	1.4325	1.4221
r_{12}^2	2.3698	0.0859	2.5416	2.5164
$\nabla_1\cdot\nabla_2$	0.0	-0.1060	-0.2121	-0.1591
$r_1\cdot r_2$	0.0	-0.0429	-0.0859	-0.0647
$\delta(r_1)$	1.7981	-0.0002	1.7977	1.8104
$\delta(r_{12})$	0.1906	-0.0574	0.0759	0.1063

a See Ref. 2.

indeed they are already quite good. All the two-electron operator expectation values are substantially improved, although, just as with the energy, the corrections may leave something to be desired. The delta function, $\delta(r_{12})$, for instance is a rather severe measure of correlation effects,[14] and it is still off by about 30%; the Hartree-Fock error is about 80%.

The vanishing of the first-order corrections for one-electron operators follows from a general "strong orthogonality" property of the first-order function.[3,5] For this particular separation of the Hamiltonian, the structure of the first-order Eq. (9a) is such that Ψ_1 is automatically insured to be strongly orthogonal to the orbital φ, i.e.,

$$I(1) = \int dV_2 \Psi_1(1,2)\varphi(2) = 0. \qquad (19)$$

This integral was actually computed and tabulated for r_1 ranging from 0.0 to 2.0 and found to be 10^{-4}–10^{-5} of the value of the Hartree-Fock orbital.

TABLE III. Energies for the helium isoelectronic sequence (in a.u.); comparison of the hydrogenic and Hartree-Fock perturbation results.

		H⁻	He	Li⁺	Be²⁺
Hartree-Fock[a]	E_1	-0.48793	-2.86168	-7.23641	-13.61130
	e_2	-0.05478	-0.04835	-0.04748	-0.04725
	e_3	0.02330	0.00741	0.00440	0.00322
	E_3	-0.51942	-2.90262	-7.27949	-13.65533
Hydrogenic[a]	E_1	-0.375	-2.75	-7.125	-13.50
	E_3	-0.52397	-2.90332	-7.27977	-13.65549
E_{exact}[b]		-0.52775	-2.90372	-7.27991	-13.65557

a See Ref. 12.
b See Ref. 2.

First-order corrections were also computed for the isoelectronic ions through $Z=4$. The energy results are given in Table III, which also includes the analogous hydrogenic perturbation results. It should be noted that the 50-term first-order function for H^- has still not converged. We estimate that there may still be an error in the energy of 0.00015 a.u., which however, does not substantially alter the conclusion that the first-order function, in an isoelectronic sequence, contains an increasingly larger portion of the correlation correction as Z increases.

The comparison with the hydrogenic perturbation results are somewhat interesting. Although our energy through first order (Hartree-Fock total energy) is better than the corresponding hydrogenic energy, the total energy through third order is worse. While the Hartree-Fock approximation provides a better starting point, the hydrogenic first-order function appears to more than make up for the initial deficiencies of the scheme, energetically at least. With regard to expectation values of other operators, the situation generally

14 J. Cooper and J. B. Martin, Phys. Rev. 131, 1183 (1963).

appears to be the other way around. Table IV lists some expectation values computed to first order in both schemes, duplicating some of the numbers of Table II. With the exception of r_1^{-1}, r_{12}^{-1} (which emphasize those regions of space important for the energy), and $r_1 \cdot r_2$, the present results are closer to the exact values. The results for one-electron operators, of course, merely reflect the superiority of the Hartree-Fock function.

Some calculations were also done on helium, using only even powers of r_{12} in the approximate first-order function (17). This is equivalent to an expansion in Legendre polynomials of the angle between r_1 and r_2, i.e., it is stimulating a configuration interaction type approximation to the first-order function. These results are given in Table V, where the S and $S+P$ notation refers to functions with no r_{12} terms and functions including only zero and second power terms, respectively. While we were not able to use sufficiently large expansions to definitely determine the angular limits, the results should be qualitatively correct. It is clear that

Table IV. Some helium expectation values through first order; comparison of the hydrogenic and Hartree-Fock perturbation calculations.

Operator	Hydrogenic[a]	Hartree-Fock	Exact[b]
r_1^{-1}	1.6875	1.6872	1.6883
r_1	0.8203	0.9272	0.9295
r_1^2	1.0488	1.1848	1.1935
r_{12}^{-1}	0.9347	0.9291	0.9458
r_{12}	1.3512	1.4325	1.4221
r_{12}^2	2.0030	2.5416	2.5164
$\nabla_1 \cdot \nabla_2$	−0.2666	−0.2121	−0.1591
$r_1 \cdot r_2$	−0.0473	−0.0859	−0.0647
$\delta(r_1)$	1.6962	1.7977	1.8104
$\delta(r_{12})$	0.0090	0.0759	0.1063

[a] See Ref. 12.
[b] See Ref. 2.

most of the first-order correction is due to angular effects.

In all these calculations, a five-term representation of the Hartree-Fock orbital was used. In particular, it was expanded in five Slater-type $1s$ orbitals (fully optimized). To determine the effect of using a cruder approximation to the Hartree-Fock, the calculations were repeated with a three-term, "single exponential" expansion of the H-F orbital. The results for ϵ_2 and ϵ_3 differed by 4 and 5 units, respectively, in the fifth place from our best values in Table I.

CONCLUSIONS

The present pilot calculations on two-electron atoms suggest that a perturbation scheme based explicitly on the Hartree-Fock model will, in first order, account for a major share of the correlation effects. The energy and expectation values (with the exception of one-electron properties) are substantially improved by the first-order

Table V. Angular limit calculations for helium.

Angular type	No. of terms in Ψ_1	ϵ_2	ϵ_3	E_3
S	16	−0.01794	0.00083	−2.87879
$S+P$	28	−0.04253	0.00413	−2.90007
All types	50	−0.04835	0.00741	−2.90262

correction. Hence, for atomic and molecular properties, this procedure may provide a reasonably good "second stage of approximation" after the Hartree-Fock.

However, if one is interested in a high degree of absolute precision, some caution may be in order. This procedure obtains 97.5% of the correlation energy for helium, corresponding to an absolute error, due to higher order effects, of 0.03 eV. Since this error will almost certainly increase with the number of electrons, a first-order treatment may well become inadequate for much larger systems than helium. Our H^- results also indicate that the higher order effects of correlation are most important for negative ions, and they would have to be explicitly taken into account to get reliable results for such properties as electron affinities.

In order to obtain definitive quantitative results, we have explicitly introduced the interelectronic coordinate, r_{12}, into the first-order trial functions. In attempting to extend this technique to larger systems, however, one gets the same three-electron integral problems as in the usual variational approaches; they are brought in by the exchange effects in the Fock operator. To avoid these integral difficulties, one would presumably have to make use of some kind of configuration interaction type approximation for Ψ_1, and it may be of some interest to examine the convergence properties of this method when applied to this perturbation scheme. Its generally slow convergence, however, seems to warrant a rather pessimistic outlook.[11,16]

APPENDIX

The matrix elements of Eq. (16) are readily reduced to sums over the conventional two-electron integrals that always arise in any variational calculation on helium, which uses r_{12} explicitly. The only operator that warrants any discussion is the Coulomb operator

[16] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

(4c), which can be written more specifically as,

$$J_\varphi(1) = r_1^{-1} \int_0^{r_1} dr_2 r_2^2 \rho(2) + \int_{r_1}^\infty dr_2 r_2 \rho(2), \quad (A1)$$

where ρ is the radial charge distribution for the s orbital. Upon inserting the expansion [Eq. (18)] for the Hartree-Fock orbital, ρ becomes

$$\rho(2) = \sum_{n,\alpha} \sum_{n',\alpha'} a_{n\alpha} a_{n\alpha'} (2\alpha)^{n+\frac{1}{2}} (2\alpha')^{n'+\frac{1}{2}}$$
$$\times [(2n)!(2n')!]^{-1/2} r_2^{n+n'-2} e^{-(\alpha+\alpha')r_2}. \quad (A2)$$

Carrying out the indicated integrations, (A1) becomes

$$J_\varphi(1) = \sum_{n\alpha} \sum_{n'\alpha'} a_{n\alpha} a_{n\alpha'} (2\alpha)^{n+\frac{1}{2}} (2\alpha')^{n'+\frac{1}{2}}$$
$$\times [(2n)!(2n')!]^{-1/2} (n+n')! (\alpha+\alpha')^{-n-n'-1}$$
$$\times \left\{ \frac{1}{r_1} - \frac{1}{r_1} e^{-(\alpha+\alpha')r_1} - \frac{\alpha+\alpha'}{n+n'} e^{-(\alpha+\alpha')r_1} \right.$$
$$\left. \times \sum_{k=0}^{n+n'-2} \frac{(n+n'-k-1)(\alpha+\alpha')^k}{(k+1)!} r_1^k \right\}. \quad (A3)$$

Matrix elements for this operator are clearly simply multiple sums over the usual helium-like integrals.