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Interaction energy between two ground-state helium atoms using many-body perturbation theory

David M. Silver
Applied Physics Laboratory, The Johns Hopkins University, Laurel, Maryland 20810

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Diagrammatic many-body perturbation theory is applied to the calculation of potential-energy curves for He_2. Both model and shifted perturbative procedures are described. The shifted scheme produces a spurious R dependence for the long-range interatomic potential in both second and third order. Variational-perturbative upper-bound methods produce energies that approach an incorrect asymptotic limit at large internuclear distances. In contrast, the model-perturbative scheme in both second and third order achieves a proper distance dependence for the He_2 potential curve. Four basis sets are employed to illustrate basis-set effects.

I. INTRODUCTION

The interaction between two ground-state helium atoms represents a relatively simple chemical system. Each atom has a pair of electrons associated with it, and the electronic problem is the prototype for interactions between two nonbonded closed-shell systems. Nevertheless, the Hartree-Fock independent-particle model is insufficient[1-3] for describing the small mutual attraction between two helium atoms in the van der Waals region. Thus, electron correlation effects must be taken into account. The diagrammatic techniques of nondegenerate many-body perturbation theory[4-6] can be applied to this problem within the algebraic approximation[7] where state functions are parametrized by expansion in a finite set of basis functions. This approach has been applied to several atoms[7-9] and molecules.[10-13] This paper reports many-body perturbative calculations for the interaction energy between two ground-state helium atoms over a wide range of internuclear separations.

A large number of calculations on He_2 have been reported previously using, for example, matrix Hartree-Fock methods,[1,14] multiconfiguration self-consistent-field approaches,[15,16] valence-bond theory,[17] configuration-interaction techniques,[18-22] and perturbative treatments.[23-29] The present work is most closely similar to several previous calculations[1,14-21] which use a similar algebraic approximation involving a basis set of atomic orbitals located at each He atom. Although the most accurate of the present results may be more accurate than some of the earlier calculations[18] by $\simeq 10^{-2}$ hartree, later calculations[15,16,19-21] have an improved accuracy of $\simeq 10^{-5}$ hartree over the present results.

The previous perturbative results are not comparable to the present work. In one type of perturbative treatment,[23] the zero-order Hamiltonian, $\mathcal{H}_0$ is taken to be that of two isolated He atoms so that the interatomic potential is the perturbation $\mathcal{H}_1$. Here the matrix Hartree-Fock Hamiltonian for the He_2 molecule is taken as $\mathcal{H}_0$, and $\mathcal{H}_1$ contains the remaining interactions corresponding to the correlation energy. In another previous type of perturbative treatment,[24] the perturbative splitting of $\mathcal{H}$ is the same as that used here; however, the contributions to the total energy of He_2 are split into intra- and interatomic correlation portions as well as a Hartree-Fock portion. Different wave functions are then used[24] for the calculation of these separate portions of the problem. In the present work, four different atomic-orbital basis sets are described; however, each one is used separately for a given calculation which includes all portions of the energy. In other previous perturbative schemes,[25,26] the zero-order wave function is constructed from wave functions representing the separated atom species. Direct perturbative calculations of long-range dispersion coefficients have also been described.[27] Finally, although the usage of a basis set is similar to the present work, another previous perturbative treatment[28] differs in its use of a random-phase approximation for summing selective diagrammatic terms in the correlation-energy series.

In light of the previous calculations[1,14-28] on He_2, the present work is not intended to compete in accuracy with previous work nor to provide further detail on the nature of the interatomic potential. Such objectives would require the use of very large basis sets. Rather, the purpose of the present work is to use the well-known properties of the He_2 system to assess the efficacy of the many-body perturbative treatment using moderately small basis sets. Of particular interest is the effect of the basis set on various perturbative energy quantities as a function of the internuclear separation.

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The physical properties that are useful in this regard are the steepness of the repulsion at short internuclear distances, the depth of the attractive well in the van der Waals region, and the asymptotic behavior at large separations. A number of experimental measurements have been performed that yield information[29-37] on these characteristics of the interatomic potential of He_2.

Some theoretical aspects of the many-body perturbation theory are briefly stated, and details of the calculations are outlined in the next section. The numerical results are presented in Sec. III and discussed in Sec. IV; some concluding remarks follow.

II. THEORETICAL AND COMPUTATIONAL ASPECTS

A. Method

The diagrammatic Rayleigh-Schrödinger perturbation expansion[4-6] through third order in the energy forms the basis of a noniterative and computationally efficient algorithm[38] for electronic-structure calculations on nondegenerate ground states of atoms and molecules. Details of the present formulation within the algebraic approximation have been given.[7]

Following previous work,[7,9,13,38] two different perturbation expansions are investigated corresponding to two choices of the reference Hamiltonian, the "model" and "shifted" schemes. In the model scheme, the Hartree-Fock operator is used as a reference Hamiltonian. In the shifted expansion, the reference operator is defined as follows:

$$\mathcal{H}_0^{\text{shifted}} = \sum_{K} |\kappa\rangle\langle\kappa|\mathcal{H}|\kappa\rangle\langle\kappa| \,, \tag{1}$$

where $\mathcal{H}$ is the total Hamiltonian and $|\kappa\rangle$ denotes an N-electron determinant formed from the orbitals, both occupied and virtual, obtained from the matrix Hartree-Fock calculation. For each of these series, the kth-order energy components ϵ_k are calculated to form the total energy through third order. The total energy through kth order is designated

$$E_k \equiv E_N + \epsilon_0 + \epsilon_1 + \cdots + \epsilon_k \,, \tag{2}$$

where E_N is the nuclear repulsion energy. The [2/1] Padé approximants are constructed and variational upper bounds E_{var} are evaluated by inserting the perturbative wave function truncated at first order, Ψ_I, into the Rayleigh quotient:

$$E_{\text{var}}(\gamma) = \langle\Psi_I(\gamma)|\mathcal{H}|\Psi_I(\gamma)\rangle / \langle\Psi_I(\gamma)|\Psi_I(\gamma)\rangle \,, \tag{3}$$

where

$$\Psi_I(\gamma) = \Phi_0 + \gamma\Phi_1 \tag{4}$$

and Φ_0 and Φ_1 are the zero- and first-order contribution to the perturbative wave function, respectively. As in previous work,[7,9,13,38] an additional variational parameter γ is included with the first-order wave function, and its optimal value is determined; the corresponding energy bound is denoted $E_{\text{var}}(\gamma_{\text{opt}})$. All two-body, three-body, and four-body contributions that enter the energy expansion through third order are included in the calculations. The use of the shifted-perturbative scheme is indicated by appending a superscript S to the corresponding energy term, e.g., E_k^S represents the total energy through kth order in the shifted scheme.

B. Basis sets

Four basis sets of real Slater orbitals are employed; these are specified in Table I. Basis set A is the "double-zeta" basis of Roetti and Clementi[39]; the remaining basis sets contain additional p or s and p functions. Even the largest of these basis sets, D, is considered to be a relatively small basis. The small size of these basis sets is disadvantageous since it limits the absolute accuracy obtainable. However, small atomic basis sets are inevitably advantageous for incorporation into multicenter molecular basis sets, where the size of a calculation can be as important as its accuracy.

Following the calculation of integrals[40] over the Slater-type orbitals, a matrix Hartree-Fock (SCF) calculation[41] and transformation[41] of integrals into integrals over the SCF orbitals is performed for each basis set. The latter integrals form the input required to calculate[38] the third-order many-body perturbative results. Since matrix Hartree-Fock orbitals are used, only doubly excited config-

TABLE I. Composition of Slater-orbital basis sets for He.

Basis set	Orbitals and exponents (bohr^{-1})
A[a]	1s (1.453 63) + 1s' (2.910 93)
B	1s + 1s' + 2p (2.4607)
C	1s + 1s' + 2p' (2.461) + 2s (1.75) + 2p'' (0.917)
D	1s + 1s' + 2p' + 2s' (1.4) + 2s'' (1.96) + 2p''

[a] Double-zeta basis of C. Roetti and E. Clementi, Ref. 39.

TABLE II. Calculated energies for the helium-atom ground state using the basis sets of Table I (energy in hartree).

Basis set	*A*	*B*	*C*	*D*
$E_{\rm SCF}$	−2.861 673	−2.861 673	−2.861 673	−2.861 673
$E^{S}_{\rm var}(\gamma_{\rm opt})$	−2.875 411	−2.895 237	−2.898 048	−2.898 206
E^{S}_{2}	−2.875 442	−2.896 376	−2.898 646	−2.898 133
E^{S}_{3}	−2.875 442	−2.895 415	−2.898 337	−2.898 483
$E^{S}_{[2/1]}$	−2.875 442	−2.895 441	−2.898 339	−2.898 487
$E_{\rm var}(\gamma_{\rm opt})$	−2.875 411	−2.895 231	−2.897 902	−2.898 099
E_{2}	−2.872 922	−2.889 247	−2.891 313	−2.891 487
E_{3}	−2.874 981	−2.894 301	−2.896 888	−2.897 084
$E_{[2/1]}$	−2.875 442	−2.895 435	−2.898 180	−2.898 378

urations enter the perturbative expansions through third order.

C. He-atom energies

For comparison purposes, the basis sets of Table I are used to calculate the energy of a ground-state helium atom. The results are given in Table II, including the matrix Hartree-Fock energy $E_{\rm SCF}$ as well as $E_{\rm var}(\gamma_{\rm opt})$, E_2, E_3, and $E_{[2/1]}$ for the shifted- and model-perturbative schemes. The accuracy of $E_{\rm SCF}$ is ~7 × 10^{-6} hartree compared to the value of −2.861 680 hartree given by Gázquez and Silverstone.[42] The correlated total energies in Table II have an accuracy of ~10^{-3} hartree compared to the results of Frankowski and Pekeris:[43] −2.903 724 hartree.

III. He_2 INTERACTION ENERGIES

The interaction energy for He_2, $\Delta E(R)$, as a function of the internuclear separation R is defined as follows:

$$\Delta E(R) \equiv E({\rm He}_2; R) - 2E({\rm He}), \tag{5}$$

where $E({\rm He}_2;R)$ is the calculated energy of the He_2 system at R and E(He) is the calculated energy of an isolated He atom. It is implicit that both $E({\rm He}_2;R)$ and E(He) in Eq. (5) correspond to precisely the same computational approximation, i.e., the same basis set and the same energy quanity. If the energy quantity has a proper dependence[4] on N, the number of electrons in the system, then $\Delta E(R)$ should approach zero in the asymptotic limit of large R; that is,

$$\lim_{R\to\infty} E({\rm He}_2; R) = 2E({\rm He}). \tag{6}$$

This property has been referred[44-48] to as "size consistency."

A. Matrix Hartree-Fock results

Interaction energies at the matrix Hartree-Fock level are given in Table III for the four basis sets of Table I. The asymptotic energy $2E_{\rm SCF}$(He) is essentially the same for each basis set since the additional *s* functions in the larger basis sets do not have a significant effect on the energy, and the *p* functions have an improper symmetry to enter the Hartree-Fock wave function for the isolated He atom.

At small R, there is a major improvement in the energy between basis sets *A* and *D*; a lowering of 158 mhartree is achieved at $R = 1$ bohr. Over the range of small R, 1–3 bohr, basis sets *C* and *D* are in close agreement. In the intermediate range of R, 3–7 bohr, all the basis sets are in close agreement; however, they show an incorrect qualitative behavior since the van der Waals attraction cannot be described at the Hartree-Fock level.[1] At large R, >7 bohr, the He_2 energies approach the correct 2He energy. The negative signs for basis sets *C* and *D* over the range 8–25 bohr indicate that the corresponding He_2 energies are less than the 2He energy by an amount less than a μhartree. This is a manifestation of the inclusion of p functions in the basis set. These functions are symmetry restricted from entering the atomic He system but are available to the diatomic He_2 and therefore give rise to the sub-μ hartree imbalance seen in Table III.

The results, using basis sets *C* and *D*, are in mutual agreement to within three significant digits over the range of R, shown in Table III. In addition, these results also agree to within three significant digits over the range of R with the SCF results reported by Kestner.[1] Similar agreement is found with the $\Delta E_{\rm SCF}$ curves reported by others.[16,19-21]

TABLE III. Matrix Hartree-Fock interaction energies ΔE_{SCF} for He_2 as a function of internuclear distance R, relative to the corresponding asymptotic energy of two He atoms.[a]

R	Basis A	Basis B	Basis C	Basis D
1.0	1090.435	1061.479	932.346	931.637
2.0	131.837	128.125	121.710	121.083
2.5	43.916	42.894	41.372	41.134
3.0	14.273	13.989	13.612	13.550
3.5	4.532	4.450	4.354	4.342
4.0	1.408	1.384	1.359	1.357
4.5	0.429	0.422	0.414	0.415
5.0	0.129	0.126	0.123	0.124
5.2	0.079	0.078	0.075	0.076
5.4	0.049	0.048	0.046	0.046
5.6	0.030	0.029	0.028	0.028
5.8	0.018	0.018	0.017	0.017
6.0	0.011	0.011	0.010	0.010
6.2	0.007	0.007	0.006	0.006
6.4	0.004	0.004	0.003	0.003
7.0	0.001	0.001	0.000	0.000
8.0	0.000	0.000	−0.000	−0.000
9.0	0.000	0.000	−0.000	−0.000
10.0	0.000	0.000	−0.000	−0.000
15.0	0.000	0.000	−0.000	−0.000
20.0	0.000	0.000	−0.000	−0.000
25.0	0.000	0.000	−0.000	−0.000
$E(2\text{ He})$[b]	−5.723 345	−5.723 345	−5.723 345	−5.723 345

[a] Interaction energy in hartree, distance in bohr.

[b] Energy in hartree.

TABLE IV. Correlated interaction energies ΔE^S for He_2 as a function of internuclear distance R, relative to the corresponding asymptotic energy of two He atoms for basis set C.[a]

R	$\Delta E^S_{\text{var}}(\gamma_{\text{opt}})$	ΔE^S_2	ΔE^S_3	$\Delta E^S_{[2/1]}$
1.0	920.098	916.514	918.540	918.470
2.0	119.353	121.488	118.797	118.743
2.5	40.852	43.927	40.405	40.287
3.0	13.733	17.440	13.351	13.175
3.5	4.686	8.893	4.356	4.127
4.0	1.784	6.358	1.497	1.224
4.5	0.898	5.751	0.648	0.339
5.0	0.648	5.726	0.429	0.090
5.2	0.613	5.770	0.405	0.056
5.4	0.594	5.826	0.398	0.038
5.6	0.586	5.888	0.400	0.030
5.8	0.583	5.953	0.407	0.027
6.0	0.583	6.018	0.417	0.028
6.2	0.585	6.082	0.429	0.031
6.4	0.588	6.144	0.441	0.034
7.0	0.598	6.317	0.477	0.045
8.0	0.609	6.557	0.526	0.059
9.0	0.616	6.746	0.564	0.067
10.0	0.620	6.896	0.593	0.072
15.0	0.627	7.338	0.680	0.082
20.0	0.630	7.556	0.724	0.088
25.0	0.633	7.686	0.751	0.091
$2E^S(\text{He})$[b]	−5.796 097	−5.797 292	−5.796 674	−5.796 679

[a] Interaction energy in mhartree, distance in bohr.

[b] Energy in hartree.

TABLE V. Correlated interaction energies ΔE^S for He_2 as a function of internuclear distance R, relative to the corresponding asymptotic energy of two He atoms for basis set D.[a]

R	$\Delta E^S_{\mathrm{var}}(\gamma_{\mathrm{opt}})$	ΔE^S_2	ΔE^S_3	$\Delta E^S_{[2/1]}$
1.0	918.597	915.220	916.883	916.879
2.0	118.686	120.232	118.179	118.079
2.5	40.500	42.879	40.105	39.933
3.0	13.572	16.561	13.247	13.009
3.5	4.598	8.043	4.326	4.031
4.0	1.705	5.476	1.474	1.136
4.5	0.829	4.994	0.658	0.264
5.0	0.579	4.969	0.443	0.016
5.2	0.544	5.013	0.422	−0.018
5.4	0.527	5.069	0.417	−0.035
5.6	0.520	5.132	0.422	−0.041
5.8	0.519	5.196	0.432	−0.041
6.0	0.521	5.261	0.445	−0.038
6.2	0.525	5.324	0.459	−0.033
6.4	0.530	5.385	0.474	−0.028
7.0	0.545	5.553	0.516	−0.012
8.0	0.562	5.777	0.570	0.007
9.0	0.572	5.947	0.610	0.018
10.0	0.578	6.086	0.641	0.025
15.0	0.589	6.517	0.735	0.040
20.0	0.595	6.727	0.782	0.047
25.0	0.598	6.852	0.810	0.051
$2E^S(\mathrm{He})$[b]	−5.796 412	−5.796 266	−5.796 966	−5.796 973

[a] Interaction energy in mhartree, distance in bohr.
[b] Energy in hartree.

TABLE VI. Correlated interaction energies ΔE for He_2 as a function of internuclear distance R, relative to the corresponding asymptotic energy of two He atoms for basis set C.[a]

R	$\Delta E_{\mathrm{var}}(\gamma_{\mathrm{opt}})$	ΔE_2	ΔE_3	$\Delta E_{[2/1]}$
1.0	920.107	918.270	918.188	918.740
2.0	119.238	118.446	118.467	118.642
2.5	40.746	40.046	40.100	40.197
3.0	13.634	13.008	13.043	13.093
3.5	4.597	4.017	4.030	4.055
4.0	1.703	1.142	1.146	1.160
4.5	0.821	0.267	0.269	0.278
5.0	0.572	0.020	0.023	0.030
5.2	0.537	−0.014	−0.011	−0.005
5.4	0.519	−0.032	−0.029	−0.023
5.6	0.510	−0.040	−0.037	−0.031
5.8	0.507	−0.042	−0.039	−0.034
6.0	0.507	−0.041	−0.038	−0.034
6.2	0.509	−0.038	−0.035	−0.031
6.4	0.512	−0.035	−0.032	−0.029
7.0	0.521	−0.024	−0.022	−0.020
8.0	0.530	−0.011	−0.010	−0.009
9.0	0.535	−0.005	−0.005	−0.004
10.0	0.538	−0.002	−0.002	−0.002
15.0	0.539	−0.000	−0.000	−0.000
20.0	0.539	−0.000	−0.000	−0.000
25.0	0.539	−0.000	−0.000	−0.000
$2E(\mathrm{He})$[b]	−5.795 804	−5.782 625	−5.793 776	−5.796 360

[a] Interaction energy in mhartree, distance in bohr.
[b] Energy in hartree.

TABLE VII. Correlated interaction energies ΔE for He_2 as a function of internuclear distance R, relative to the corresponding asymptotic energy of two He atoms for basis set D.[a]

R	$\Delta E_{\rm var}(\gamma_{\rm opt})$	ΔE_2	ΔE_3	$\Delta E_{[2/1]}$
1.0	918.460	916.740	916.487	916.997
2.0	118.616	117.843	117.855	118.023
2.5	40.460	39.766	39.815	39.911
3.0	13.538	12.905	12.943	12.996
3.5	4.567	3.974	3.994	4.024
4.0	1.684	1.108	1.120	1.139
4.5	0.801	0.233	0.241	0.256
5.0	0.553	−0.011	−0.003	0.008
5.2	0.519	−0.044	−0.036	−0.025
5.4	0.502	−0.059	−0.051	−0.042
5.6	0.495	−0.064	−0.057	−0.049
5.8	0.494	−0.064	−0.057	−0.049
6.0	0.496	−0.060	−0.054	−0.047
6.2	0.499	−0.055	−0.049	−0.043
6.4	0.504	−0.049	−0.044	−0.039
7.0	0.516	−0.033	−0.029	−0.026
8.0	0.530	−0.015	−0.013	−0.011
9.0	0.537	−0.006	−0.005	−0.005
10.0	0.539	−0.002	−0.002	−0.002
15.0	0.541	−0.000	−0.000	−0.000
20.0	0.541	−0.000	−0.000	−0.000
25.0	0.541	−0.000	−0.000	−0.000
$2E$(He)[b]	−5.796 198	−5.782 974	−5.794 169	−5.796 756

[a] Interaction energy in mhartree, distance in bohr.
[b] Energy in hartree.

B. Correlated results using the shifted perturbative scheme

Interaction energies derived from the shifted perturbative scheme are given in Tables IV and V for basis sets C and D of Table I. Over the range of small R, 1–3 bohr, the results using basis sets C and D are in reasonably close agreement. In the range $R > 3$ bohr, all of the results show incorrect behavior. The Padé results $\Delta E^{S}_{[2/1]}$ for basis set D exhibit an attractive well; however, even in this case, the behavior at large R is incorrect.

C. Correlated results using the model-perturbative scheme

Interaction energies derived from the model-perturbative scheme are given in Tables VI and VII for basis sets C and D of Table I. The interaction energy from the variational procedure, $\Delta E_{\rm var}(\gamma_{\rm opt})$, exhibits an incorrect dependence on R and approaches an incorrect asymptotic limit similar to the situation found with the shifted scheme. However, the quantities ΔE_2, ΔE_3, and $\Delta E_{[2/1]}$ in the model scheme each approach the correct asymptotic limit at large R and exhibit reasonable behavior as a function of R as the basis sets are improved. Basis set A contains only s orbitals, and it is not capable of producing a van der Waals minimum. Basis set B, with an additional p function per atom, shows only a slight improvement in this respect. Basis sets C and D, however, appear to have enough flexibility to produce proper R dependencies in the model-perturbative energy quantities. In addition, ΔE_2, ΔE_3, and $\Delta E_{[2/1]}$ for basis sets C and D are in good mutual agreement with one another in the repulsive region, $R \leq 4.5$ bohr.

IV. DISCUSSION

A. Variational-perturbative upper bounds

Although the variational energies, $E_{\rm var}$ in Eq. (3), represent rigorous upper bounds to the true energy eigenvalue over the entire potential curve, the interaction energies $\Delta E_{\rm var}$ are defined to be energy differences and do not represent rigorous upper bounds. The unavoidable loss of the upper-bound property in forming $\Delta E_{\rm var}$ is itself not an impediment to its usefulness. However, $\Delta E_{\rm var}$ does have an undesirable property, namely, that $\Delta E_{\rm var}$ approaches a wrong asymptotic limit at large R for both the shifted- and model-perturbative schemes as seen in Tables IV–VII. This behavior is due to the unlinked-cluster effect.

Inserting the perturbative wave function truncated at first order, Ψ_I of Eq. (4) with γ chosen to be unity, the Rayleigh quotient of Eq. (3) has the form

$$\Delta E_{\text{var}}(\gamma=1)=E_{\text{SCF}}+(\epsilon_2+\epsilon_3)/(1+S_{11}), \qquad (7)$$

where S_{11} is the self-overlap of the first-order contribution to the perturbative wave function:

$$S_{11}=\langle\Phi_1|\Phi_1\rangle . \qquad (8)$$

The various perturbative terms have the asymptotic values

$$\lim_{R\to\infty}\epsilon_k(\text{He}_2)=2\epsilon_k(\text{He}), \qquad (9)$$

$$\lim_{R\to\infty}S_{11}(\text{He}_2)=2S_{11}(\text{He}). \qquad (10)$$

The asymptotic value for S_{11}, although correct, causes ΔE_{var} in Eq. (7) to have a wrong asymptotic value. Using Eqs. (9) and (10) and expanding the denominator in Eq. (7) shows that $\lim_{R\to\infty}\Delta E_{\text{var}}(\text{He}_2)$ is the correct through third order but has higher-order errors beginning with the fourth-order unlinked-cluster[4] factor $\epsilon_2 S_{11}$.

The variational parameter γ in the perturbative wave function of Eq. (4) gives added flexibility:

$$\begin{aligned} E_{\text{var}}(\gamma) &= E_{\text{SCF}}+\frac{(2\gamma-\gamma^2)\epsilon_2+\gamma^2\epsilon_3}{1+\gamma^2 S_{11}} \\ &\equiv E_{\text{SCF}}+\gamma_{\text{opt}}\epsilon_2 , \end{aligned} \qquad (11)$$

where the variationally optimal value of γ is given by

$$\begin{aligned} \gamma_{\text{opt}} &= S_{11}^{-1}[(\zeta^2+S_{11})^{\frac{1}{2}}-\zeta], \\ \zeta &= \tfrac{1}{2}(1-\epsilon_3/\epsilon_2). \end{aligned} \qquad (12)$$

Using Eqs. (9) and (10), the asymptotic value of γ_{opt} for He_2 differs from γ_{opt} for He as follows:

$$\begin{aligned} &\lim_{R\to\infty}\gamma_{\text{opt}}(\text{He}_2)-\gamma_{\text{opt}}(\text{He}) \\ &\qquad = -S_{11}(\text{He})/(8\zeta^3)+O[S_{11}^2(\text{He})/\zeta^5]. \end{aligned} \qquad (13)$$

Thus $\Delta E_{\text{var}}(\gamma)$ in Eq. (11) has an asymptotic error again of fourth order involving the unlinked-cluster factor $\epsilon_2 S_{11}$ as the leading term.

The magnitude of the fourth-order unlinked-cluster problem in He_2 is of the order of ~0.5 mhartree as seen in Tables IV–VII. For the He_2 potential curve, this is a serious error. For other chemical systems, the importance of this effect would need to be determined since (a) the error would have a value characteristic of the species involved, and (b) the degree of accuracy required for any given system is also species dependent. Nevertheless, since the error is present formally, there must be numerical errors in the asymptotic behavior of all interaction potentials calculated using ΔE_{var}. Moreover, since the rigorous upper-bound quality of E_{var} is lost upon forming ΔE_{var}, the perturbative upper-bound energies are not totally satisfactory for describing the behavior of an entire interaction-energy curve.

B. Perturbative results for large R

The shifted-perturbative results, ΔE_2^S, ΔE_3^S, and $\Delta E_{[2/1]}^S$ in Tables IV and V, exhibit a remarkable property, namely, that the behavior of these interaction energies for large R is incorrect. Compared to the error present in $\Delta E_{\text{var}}^S(\gamma_{\text{opt}})$, the errors for ΔE_2^S, ΔE_3^S, and $\Delta E_{[2/1]}^S$ are, respectively, an order of magnitude greater than, comparable to, and an order of magnitude less than the error found in $\Delta E_{\text{var}}^S(\gamma_{\text{opt}})$. In contrast, the interaction energies ΔE_2, ΔE_3, and $\Delta E_{[2/1]}$ derived from the model-perturbative scheme do not share this deleterious feature.

Of the shifted-perturbative results, perhaps the most reasonable is obtained from basis set D in Table V since $\Delta E_{[2/1]}^S$ for basis set D displays proper behavior in the short-range and van der Waals regions. Thus basis set D is chosen for a more detailed analysis, and comparison between the shifted- and model-perturbative schemes, in particular, over the range of $R\geq 6$ bohr where an R dependence on the order of $-aR^{-6}$ should dominate the total energies.

The R dependence of E_N, ϵ_0, and ϵ_1 for basis set D is shown in Fig. 1. The E_N curve is, of course, simply proportional to R^{-1} and has a variation of -0.27 hartree over the interval from 6–10 bohr. By comparison, ϵ_0 varies only -30 μhartree over this interval. However, ϵ_1 is proportional to $-R^{-1}$ in this interval and has a variation comparable but opposite in sign to E_N. Thus, the sum of these three terms, E_{SCF}, has only a slight R dependence with a variation of -10 μhartree over the 6–10 bohr interval. The second-

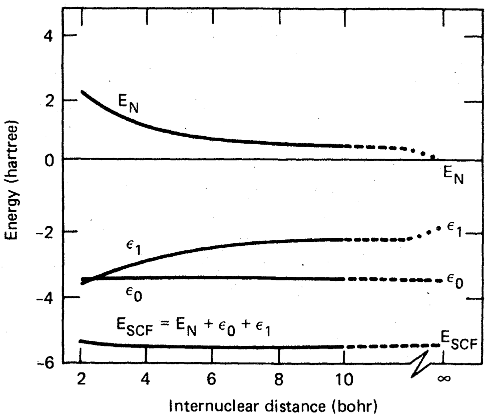

FIG. 1. Perturbative energy contributions for He_2 as a function of internuclear distance using basis set D of Table I: E_N is the nuclear repulsion energy; ϵ_0 and ϵ_1 are the zero- and first-order perturbative terms. The curves are extrapolated to the points on the right corresponding to energies for 2He.

and third-order energies are shown in Fig. 2.

To give some indication of the R dependence of various curves in Figs. 1 and 2, over the range 6–10 bohr, a fitting of the curves to the three-parameter function

$$y = y_0 \pm C_n R^{-n} \tag{14}$$

has been performed using energy values at 6, 8, and 10 bohr. As a check on the fitting procedure, it has also been applied to the potential curve of Siska *et al.*[32] (which they denote as ESMSV) which has the explicit analytical form

$$V(R) = C_6 R^{-6} + C_8 R^{-8} + C_{10} R^{-10}, \tag{15}$$

with $C_6 = -1.45$ hartree bohr^6, $C_8 = -14.0$ hartree bohr^8, and $C_{10} = -180$ hartree bohr^{10}. Fitting Eq. (15) to the simpler form of Eq. (14) over the range 6–10 bohr gives $C_n - 4.09$ hartree bohr^n and $n = 6.41$. It is clear that this fitting scheme is crude; nevertheless, it should be useful for identifying the proper range of the exponent of R for potential curves of widely separated R dependencies. Results are given in Table VIII where ϵ_k and E_k are defined in Eq. (2).

Although E_N and ϵ_1 both are of the form R^{-1}, their coefficients C_n are approximately equal but of opposite sign. Hence, the R^{-1} dependence is largely canceled; the effect of the residual R dependence can be seen by comparing n for $\epsilon_2 + \epsilon_3$ with n for E_3 in Table VIII.

TABLE VIII. Approximate fit of the potential curves for basis set D to the form $y = y_0 \pm C_n R^{-n}$ using the calculated energy values at 6, 8, and 10 bohr.[a]

Energy	y_0[b]	C_n	n
E_N	0.000 000	4.00	1.00
ϵ_1	−4.103 116	−4.00	1.00
$\epsilon_0 + \epsilon_1$	−5.723 345	−4.00	1.00
ϵ_2	−0.059 629	−9.29	6.58
ϵ_3	−0.011 195	4.20	7.49
$\epsilon_2 + \epsilon_3$	−0.070 823	−7.47	6.51
E_3	−5.794 169	−3.44	6.17
ϵ_3 (diagonal)	−0.005 378	−0.0082	0.90
ϵ_3 (diagonal-PP)	+0.003 329	0.0042	0.92
ϵ_3 (diagonal-HP)	−0.013 930	−0.0176	0.94
ϵ_3 (diagonal-HH)	+0.005 223	0.0053	1.02
ϵ_2^S	(−0.065 610)	−0.0128	1.02
ϵ_3^S	(−0.007 350)	0.0080	0.82
$\epsilon_2^S + \epsilon_3^S$	(−0.072 816)	−0.0064	1.59
E_3^S	(−5.796 110)	−0.0040	1.26
$E_{\mathrm{var}}(\gamma_{\mathrm{opt}})$	(−5.795 657)	−2.49	6.10
$E_{\mathrm{var}}^S(\gamma_{\mathrm{opt}})$	(−5.795 814)	−0.0087	2.64

[a] y_0 and C_n are in hartree.

[b] y_0 is taken to be $2E(\mathrm{He})$ corresponding to $E(\mathrm{He}_2)$ except for the shifted terms and E_{var} where y_0 (in parentheses) corresponds to a "best fit" to Eq. (14).

The second-order energy ϵ_2 has the form

$$\epsilon_2 = \sum_{i<j} \sum_{a<b} \langle ij \| ab \rangle \langle ab \| ij \rangle / D(ijab), \tag{16}$$

where i, j denote occupied and a, b denote unoccupied matrix Hartree-Fock spin orbitals φ_p and

$$\langle pq \| rs \rangle = \int d\tau_1 \int d\tau_2 \varphi_p(1) \varphi_q(2) \times r_{12}^{-1} [\varphi_r(1)\varphi_s(2) - \varphi_s(1)\varphi_r(2)]. \tag{17}$$

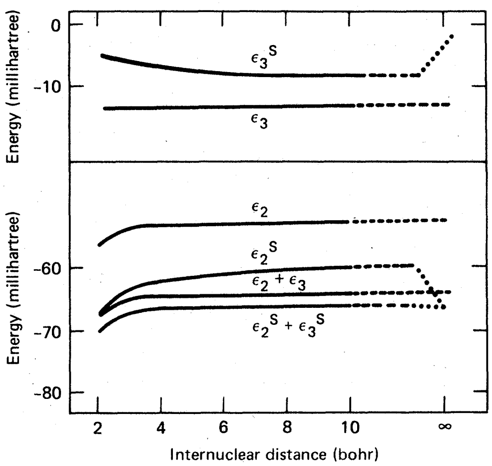

FIG. 2. Perturbative energy contributions for He_2 as a function of internuclear distance using basis set D of Table I: ϵ_2 and ϵ_3 are model energies; ϵ_2^S and ϵ_3^S are shifted energies. The curves are extrapolated to the points on the right corresponding to energies for 2He.

The denominators

$$D(pqrs) = e_p + e_q - e_r - e_s \tag{18}$$

depend on the orbital energies e_p. The occupied

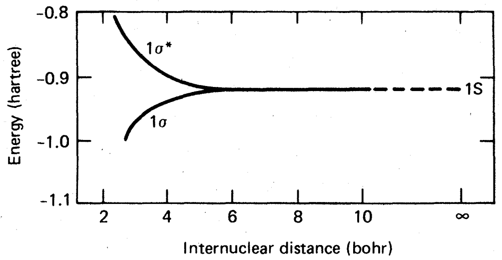

FIG. 3. Occupied orbital energies for He_2 using basis set D, extrapolated to the corresponding $1S$ orbital energy of He.

e_i are shown in Fig. 3 and the unoccupied e_a are shown in Fig. 4. The overall $\sim R^{-6.6}$ dependence must arise from a balance between the R dependencies of the $D(ijab)$ and the corresponding $\langle ij||ab\rangle$ integrals.

The shifted second-order energy ϵ_2^S is similar to Eq. (16) except that the denominators are shifted:

$$D^S(ijab) = D(ijab) - \Delta^S(ijab)\,, \tag{19}$$

where

$$\Delta^S(ijab) = \langle ab||ab\rangle + \langle ij||ij\rangle + \langle ai||ia\rangle + \langle bi||ib\rangle + \langle aj||ja\rangle + \langle bj||jb\rangle\,. \tag{20}$$

If the denominator D^S $(ijab)$ is expanded in ϵ_2^s, then

$$\epsilon_2^S = \epsilon_2 + \epsilon_3(\text{diagonal}) + \epsilon_4(\text{diagonal}) + \cdots\,, \tag{21}$$

where the third-order diagonal terms are as follows:

$$\epsilon_3(\text{diagonal}) = \epsilon_3(\text{particle-diag}) + \epsilon_3(\text{ring-diag}) + \epsilon_3(\text{hole diag})\,, \tag{22}$$

$$\epsilon_3(\text{particle-diag}) = \sum_{i<j}\sum_{a<b} \langle ij||ab\rangle\langle ab||ab\rangle\langle ab||ij\rangle/[D(ijab)]^2\,, \tag{23}$$

$$\epsilon_3(\text{ring-diag}) = \sum_{i<j}\sum_{a<b} \langle ij||ab\rangle\,(\langle ai||ia\rangle + \langle bi||ib\rangle + \langle aj||ja\rangle + \langle bj||jb\rangle)\langle ab||ij\rangle/[D(ijab)]^2\,, \tag{24}$$

$$\epsilon_3(\text{hole-diag}) = \sum_{i<j}\sum_{a<b} \langle ij||ab\rangle\langle ij||ij\rangle\,\langle ab||ij\rangle\,/[D(ijab)]^2\,. \tag{25}$$

These diagonal terms are shown in Fig. 5, and their R dependence is $\sim R^{-0.9}$ to $R^{-1.0}$ from Table VIII. Inclusion of these and higher-order diagonal terms in ϵ_2^S by means of the denominator shift gives rise to the $\sim R^{-1}$ dependence for ϵ_2^S.

Since ϵ_3 (diagonal) has an $\sim R^{-0.9}$ dependence and ϵ_3 has $\sim R^{-7.5}$, it follows that the nondiagonal contributions

$$\epsilon_3(\text{nondiagonal}) = \epsilon_3 - \epsilon_3(\text{diagonal}) \tag{26}$$

must also have an R dependence of $\sim R^{-0.9}$, but of opposite sign to ϵ_3(diagonal), so that a cancellation can occur on adding these two components to form ϵ_3 with its observed $\sim R^{-7.5}$ residual.

The shifted third-order energy ϵ_3^S consists of ϵ_3(nondiag), having an R dependence of $\sim R^{-0.9}$, plus higher-order contributions that arise from the shifted denominator. The net result for ϵ_3^S is to produce an $\sim R^{-0.8}$ dependence. The sum of shifted energies through third order has the form

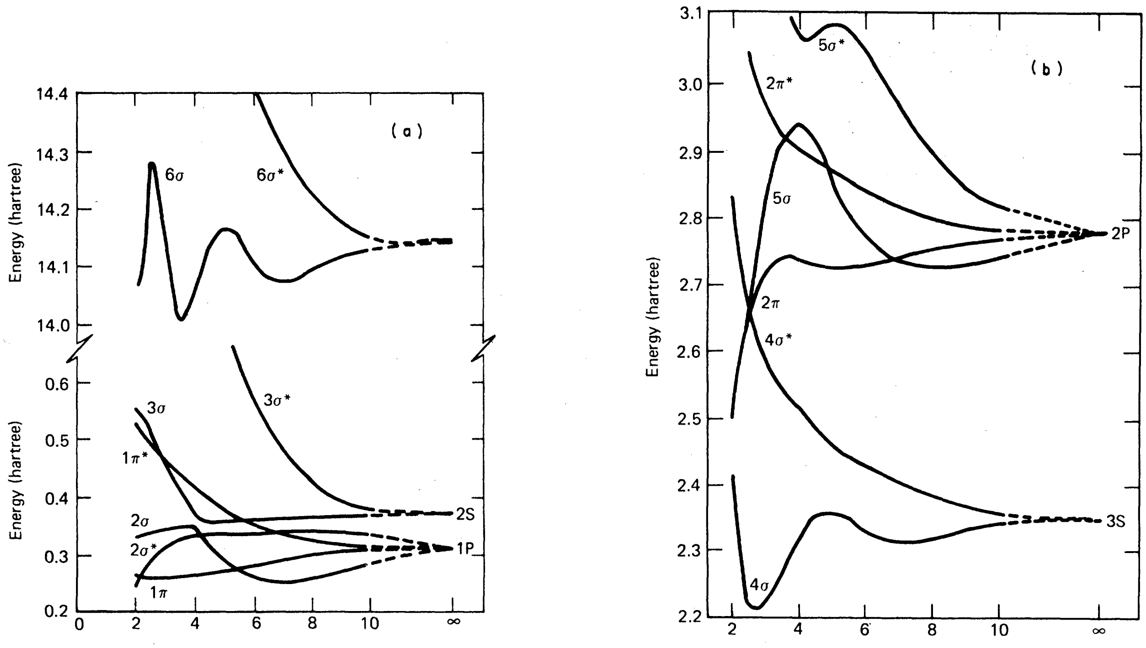

FIG. 4. (a) and (b): Unoccupied orbital energies for He_2 using basis set D, extrapolated to corresponding orbital energies of He.

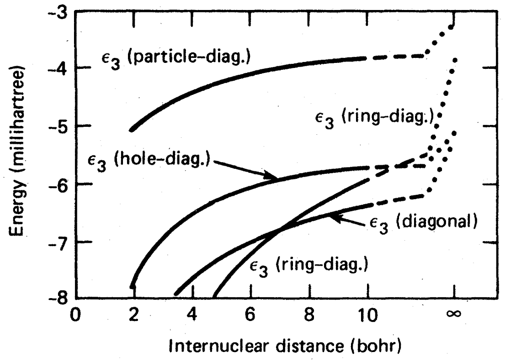

FIG. 5. Diagonal contributions to the third-order energy defined in Eqs. (22)–(25) using basis set D. The curves are extrapolated to the points on the right corresponding to energies for 2He.

$$\epsilon_2^S + \epsilon_3^S = \epsilon_2 + \epsilon_3 + \cdots , \tag{27}$$

where the ⋯ represents higher-order diagonal-type terms. Since the shifted sum $\epsilon_2^S + \epsilon_3^S$ goes as $\sim R^{-1.6}$ while the model sum $\epsilon_2 + \epsilon_3$ goes as $\sim R^{-6.5}$, the higher-order terms included in the shifted sum exert an important (although deleterious) influence on the shifted energy.

In passing, the same fitting procedure can of course be applied to $E_{\mathrm{var}}(\gamma_{\mathrm{opt}})$. The result is given in Table VIII and shows that although the asymptotic value to which the model $E_{\mathrm{var}}(\gamma_{\mathrm{opt}})$ approaches is incorrect, the dependence on R over the range 6–10 bohr is of the right order, $\sim R^{-6.1}$. In contrast, the shifted $E_{\mathrm{var}}^S(\gamma_{\mathrm{opt}})$ has a dependence of $\sim R^{-2.6}$ which is less than desirable.

C. Perturbative results for $R < 7$ bohr

The model-perturbative energies ΔE_2, ΔE_3, and $\Delta E_{[2,1]}$ are well behaved in the region of large R. Therefore it is of interest to examine their characteristics at shorter range, especially for basis sets C and D. Therefore, the data in Tables VI and VII have been fit to the following forms[32]:

$$f(x) = \begin{cases} \Delta E(R)/\epsilon , \quad x = R/R_m & (28) \\ A \exp[-\alpha(x-1)], \quad 1 \leqslant R \leqslant 3 & (29) \\ \exp[-2\beta(x-1)] - 2\exp[-\beta(x-1)], & \\ \qquad\qquad 4.5 \leqslant R \leqslant 6.4 . & (30) \end{cases}$$

The resulting parameters are given in Table IX along with some previous determinations[32] of these parameters for other He_2 potential curves.

The basis sets C and D are both relatively small and consequently somewhat incomplete. The effect of this incompleteness is manifest in the variations seen for the parameters in Table IX on going from basis C to D and by comparison with the previous results. Nevertheless, for each parameter determined, there is a monotonic progression along the sequence ΔE_2, ΔE_3, $\Delta E_{[2,1]}$.

Potential curves are drawn for ΔE_3 for basis sets C and D in Fig. 6. The short-range repulsive nature of the two curves appears to be quite similar, whereas the attractive well appears to be substantially different along the two curves. However, this view of the relative behavior of the two potentials could be misleading. In absolute terms, as is evident from Tables VI and VII, there is more deviation at short R between the energies calculated with the two basis sets than there is in the

TABLE IX. Parameters for He_2 interatomic potentials corresponding to Eqs. (28)–(30).

Potential	α	A	β	ϵ (μh)	R_m(bohr)
Basis set C					
ΔE_2	11.92	1.120	5.87	42.6	5.79
ΔE_3	11.93	1.198	5.97	39.4	5.79
$\Delta E_{[2/1]}$	12.00	1.281	6.09	34.6	5.83
Basis set D					
ΔE_2	11.69	0.929	5.56	65.4	5.66
ΔE_3	11.72	1.003	5.69	58.2	5.68
$\Delta E_{[2/1]}$	11.80	1.078	5.82	50.1	5.72
Previous results					
expt [a]	15.058	0.343	6.475	33.5	5.61
ESMSV [b]	12.53	0.684	6.58	37.8	5.59
MSV [b]			6.2	52.7	5.48
MCSCF [c]				36.0	5.60
CI [d]				38.0	5.6

[a] Experimental results of Burgmans, Farrar, and Lee, Ref. 37.
[b] Potential curves described by Siska *et al.*, Ref. 32.
[c] Bertoncini and Wahl, Ref. 15.
[d] Schaefer *et al.*, Ref. 19.

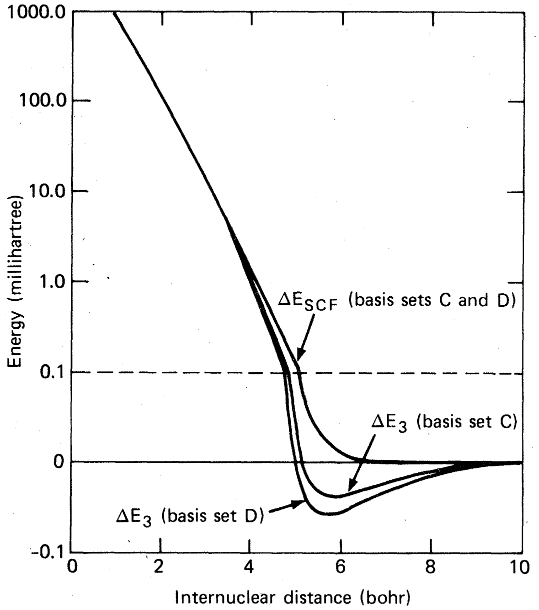

FIG. 6. Third-order interaction potentials for He_2 using the model-perturbative scheme. A linear scale is used for energies below 10^{-4} hartree and a logarithmic scale for energies above 10^{-4} hartree.

region of the well.

By comparison with the previous results in Table IX, the depth of the well ϵ obtained with basis set D appears to be overestimated. Basis set D is apparently more adequate for the He_2 molecule than it is for the isolated He atoms. To some extent, basis set C is better balanced in this regard. The use of much larger basis sets can reduce this problem by approaching "completeness" in the basis for both the separated atoms and the molecule.[21] Other schemes have also been discussed.[49]

V. CONCLUSIONS

The present calculations shed some light on the differences between the model- and shifted-perturbative schemes. For He_2, where it is mandatory to take account of electron correlation effects, it appears that proper distance dependence can be achieved in an interatomic potential curve obtained with the model scheme in both second and third order. In contrast, the shifted scheme produces interatomic potentials with a spurious long-range R dependence($\sim R^{-1}$) in both second and third order. It is particularly disappointing that the shifted-perturbative scheme displays this difficulty for the He_2 system since this is an application of nondegenerate perturbation theory to a strictly nondegenerate problem. The difficulty in the shifted scheme arises because the shifted denominators have the effect of including only the diagonal portions of higher-order terms in a low-order calculation. This upsets a necessary balance between diagonal and nondiagonal contributions to the perturbative energy series. These observations certainly argue heavily in favor of the model-perturbative scheme.

As is well known, the variational-perturbative upper-bound procedure introduces certain unlinked-cluster terms in the energy expression. This leads to an incorrect asymptotic energy for the He_2 system on the order of ~ 0.5 mhartree. To avoid this difficulty, a linked-cluster approach such as the model-perturbative scheme is again recommended.

The size and content of a basis set exert a strong influence on the results of electronic-structure calculations. In principle, basis-set effects can be eliminated and high accuracy achieved through the use of a "complete" set of basis functions. In the absence of a genuine complete set, one alternative would be to use a large well-distributed set of atomic orbitals such as that described recently as a universal basis set.[50] Nevertheless, even in circumstances which approach basis set completeness, the fundamental difficulties of the shifted-perturbative scheme and the variational-perturbative upper bound are expected to remain.

It is interesting that the problems of asymptotic separated-atom limits and long-range internuclear-distance dependence are truly "molecular problems" that do not occur in an isolated atomic problem. Although the unlinked-cluster effect on ΔE_{var} was anticipated in advance of these calculations, the R-dependence problem arising in the shifted-perturbative scheme is an unanticipated result of numerical explorations.

Malrieu and Spiegelmann[51] have recently described a similar occurrence of an artifactual R dependence in the long-range portion of a diatomic potential curve using the shifted-perturbative scheme with canonical matrix Hartree-Fock orbitals as the occupied set. A transformation to localized molecular orbitals eliminates the spurious R dependence in the shifted-perturbative scheme. The model- or unshifted-perturbative scheme does not exhibit spurious R dependence and is invariant to a transformation to localized occupied orbitals.

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