

CALCULATION OF THE ATTRACTIVE He PAIR POTENTIAL*

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The symmetry-adapted pair-correlation energy of diatomic helium was evaluated for five internuclear separations near the potential minimum by means of localized orbitals obtained from transformation of a molecular Hartree-Fock wave function. An attractive potential depth of 12.0°K at $R=2.96$ Å was obtained in agreement with the best experimental estimates, leading to the conclusion that the omitted electron correlation within the helium atom does not affect the interatomic correlation energy by more than about 10%. This result is in essential agreement with that obtained independently by Bertoncini and Wahl. The electron correlation contribution is divided into σ , π , and δ parts as well as into its atomic symmetry so as to elucidate the magnitude of the various contributions.

The theoretical prediction and experimental determination of the He-He interaction potential near the van der Waals minimum are problems of continuing interest.¹⁻⁴ Among the various theoretical methods applied to He₂, the localized pair correlation approach^{5,6} appears to be one of the most promising, since it deals accurately with atoms and hence should do well for weakly interacting atoms. Previous pair-correlation calculations^{5,6} of the He-He potential curve did not use sufficiently large basis sets nor the sum of symmetry-adapted pair-correlation energies which was recently found⁷ to represent an improved approximation to the total electron correlation energy of a many-electron atomic system. In this communication we present the first results of a series of extensive calculations of the symmetry-adapted pair-correlation energies of the He₂ molecule near the van der Waals minimum.

Theoretical approach.—As the name of the method implies, the correlation energy E_c of an atom or molecule is approximated by a sum of independently computed pair-correlation energies,⁸ $e(i, j)$:

$$E_c \approx \sum_{i,j} e(i, j).$$

In most studies,⁹ the "pair correlations" refer to correlations between all pairs of canonical Hartree-Fock (HF) spin orbitals in the presence of a fixed HF sea. However, for closed-shell systems, the HF wave function is invariant to unitary transformations among the HF orbitals, and other choices of reference-state orbitals can be made for pair-correlation studies.¹⁰ Such a transformation to the separate-atom basis is particularly useful for the weakly interacting He-He case. Thus, if the HF orbitals ($1\sigma_g$ and $1\sigma_u$) are transformed to localized orbitals¹¹ ($1\sigma_A$ and $1\sigma_B$) then the $1\sigma_A^2$ and $1\sigma_B^2$ pair correla-

tions approximately correspond to the correlation energy of two isolated helium atoms. The $1\sigma_A 1\sigma_B$ correlation, added to the HF energy, is then anticipated⁶ to describe the He-He interaction near the van der Waals minimum quite accurately.

In the usual procedures^{5,6,9} the four pair-correlation energies $1\sigma_A \alpha 1\sigma_B \alpha$, $1\sigma_A \alpha 1\sigma_B \beta$, $1\sigma_A \beta 1\sigma_B \alpha$, and $1\sigma_A \beta 1\sigma_B \beta$ are independently computed and summed to get the correlation contribution to the van der Waals interaction. However, such a formulation of pair correlations in terms of spin orbitals will not yield pair-correlation wave functions which are eigenfunctions of $\hat{S}^2$. For the neon atom, it has been shown^{7,12} that the sum of the usual pair-correlation energies yields ~110% of the correlation energy, while the sum of the symmetry-adapted pair correlations yields the correlation energy with a 1% accuracy.⁷ In the symmetry-adapted treatment of He-He, a single pair-correlation energy $e(1\sigma_A, 1\sigma_B)$ represents the contribution of electron correlation to the van der Waals interaction. By including in a single calculation all the Slater determinants required to compute the usual four pair correlations, it is possible to obtain an exact eigenfunction of $\hat{S}^2$.

Calculations.—First of all, very accurate Hartree-Fock wave functions for the He-He molecule were computed. To this end the diatomic self-consistent field (SCF) program BISON of Wahl and co-workers¹³ was employed. After a great deal of basis-set experimentation, a set of five 1s, two 2p (with orbital exponents $\zeta = 1.0$, 2.0), and one 3d ($\zeta = 1.2$) Slater-type orbitals (STO's) was used. The five 1s functions are those optimized in an SCF calculation on the ground state of the He atom.¹⁴ The SCF wave functions thus computed are estimated to lie no more than 1×10^{-6} hartree above the true molec-

Table I. Optimized Slater-type orbitals for diatomic helium at $R = 5.6$ bohrs.

Type	Orbital exponent
2s	1.3
3s	1.3
2p	1.6
3p	1.6
3d	1.3
4d	1.3
4f	1.0

ular Hartree-Fock energy. The HF orbitals were localized by symmetry:

$$1\sigma_A = (1/\sqrt{2})[1\sigma_g + 1\sigma_u],$$

$$1\sigma_B = (1/\sqrt{2})[1\sigma_g - 1\sigma_u],$$

and the localized orbitals $1\sigma_A$ and $1\sigma_B$ were held fixed for the ensuing configuration-interaction calculations and treated¹⁵ as numerical orbitals. The subsequent correlation-energy calculations were made possible by recently developed numerical and computational methods for the calculation of molecular integrals¹⁵ and for the construction of diatomic symmetry-adapted configurations.¹⁶

To optimize STO's for the electron correlation, calculations of $e(1\sigma_A, 1\sigma_B)$ were carried out using only s orbitals, only p orbitals, only d orbitals, and only f orbitals. For $R = 5.6$ bohrs, the optimized STO's are given in Table I. Exponent optimization was carried out at each internuclear separation. A point of interest concerning the optimized exponents is that they lie about halfway between those required to correlate the He-atom ground state [$\zeta(2p) \sim 2.5$] and those required to describe the excited states of He [for $1s2p$ states, $\zeta(2p) \sim 0.5$]. The basis set of Table I is close to completeness. The most important function not included is an additional p function,

which added 0.6% to the correlation contribution from p orbitals.

Results.—Because of the $^1\Sigma^+$ molecular symmetry, only a limited number of types of configurations can arise. These types and their numbers resulting from the basis set of Table I are as follows:

Configuration	Number
$1\sigma_A 1\sigma_B \sigma_i \sigma_j$	210
$1\sigma_A 1\sigma_B \pi_i \pi_j$	100
$1\sigma_A 1\sigma_B \delta_i \delta_j$	36

In most of the calculations reported here, $e(1\sigma_A, 1\sigma_B)$ is approximated as a sum of three separate contributions; namely, those from σ , π , and δ orbitals. This approximation appears to overestimate the true $e(1\sigma_A, 1\sigma_B)$ derived from a single sum by $\sim 0.1^\circ\text{K}$. The results are summarized in Table II.

A fourth-order polynomial fit through the five data points leads to a maximum well depth of 11.97°K at 5.58 bohrs, or 2.96 Å. Most experimentally based estimates¹⁻³ of the equilibrium internuclear separation lie very close to this value, but the same estimates of the well depth are usually $\sim 10^\circ\text{K}$. However, one recent analysis¹⁷ yielded a value of $12.5 \pm 1.2^\circ\text{K}$.

Concurrent with the work reported here, Bertoncini and Wahl¹⁸ have carried out multiconfiguration SCF calculations of the van der Waals interaction in He-He. They used a smaller basis set and obtained a well depth of 10.5°K at $R = 5.66$ bohrs. Thus the two calculations are in essential agreement.

It is perhaps even more important than obtaining a reasonable He-He potential curve to be able to provide information on the origin of the van der Waals minimum. We have carried out a large number of additional calculations to provide such information. The following table gives the results of a breakdown of the correlation calculation at $R = 5.6$ bohrs in terms of atomic sym-

Table II. He-He energies at five distances.

R (bohrs)	SCF energy (hartrees)	SCF repulsion (°K)	Correlation (°K)	Total (°K)
5.2	-5.723 282 52	+24.4	-33.7	-9.2
5.4	-5.723 312 34	+15.0	-26.3	-11.3
5.6	-5.723 330 73	+9.2	-21.2	-12.0
5.8	-5.723 342 05	+5.6	-16.8	-11.2
6.0	-5.723 349 01	+3.5	-13.6	-10.1
∞	-5.723 359 94	0.0	0.0	0.0

metry:

s orbitals only	0.2°K
p orbitals only	15.7°K
d orbitals only	0.7°K
f orbitals only	0.2°K
Sum	16.8°K
$e(1\sigma_A, 1\sigma_B)$	21.2°K

It is seen that the sum of the contributions from s , p , d , and f orbitals is 4.4°K less than that obtained using s , p , d , and f orbitals simultaneously. Thus 4.4°K is a quantitative measure of the effects of mixing of different atomic angular terms. An excitation of the type $1\sigma_A 1\sigma_B \rightarrow 2p_A 3d_B$ is an example of such mixing. The C_6/R^6 term commonly discussed in treatments of intermolecular forces¹⁹ is essentially equivalent to the entry labeled " p orbitals only" in the above table. While the C_6 term is very large, the remaining 5.5°K of the well depth is not included in this term.

Table III provides a breakdown of the correlation energy which does account for the entire interaction. It is seen that the addition of d orbitals to the basis adds 4.4°K to the interaction. Only 0.7°K of this, as seen in the table in the preceding paragraph, comes from dd terms. Therefore about 3.7°K arises from sd and, primarily, pd terms. Similarly the addition of f functions adds 0.6°K, of which only 0.2°K arises from ff terms. It is clear from Table III that the calculation has converged both in terms of atomic ($s, p, d, f, \dots$) and molecular ($\sigma, \pi, \delta, \dots$) symmetries.

The preliminary calculation reported here based on HF orbitals neglects electron correlation within the He atom which is three orders of magnitude greater than the van der Waals interaction itself. Nevertheless, the above comparison with experiment seems to imply that the He-atom correlation has relatively little effect

Table III. Breakdown of the He-He correlation-energy contributions at $R=5.6$ bohrs, in °K.

	σ	π	δ
s	0.2	...	...
$s+p$	10.7	5.4	...
$s+p+d$	13.1	7.4	0.02
$s+p+d+f$	13.4	7.7	0.03

on the attractive part of the He-He potential.

We intend to carry out additional calculations to investigate this particular point.

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