<u>AB INITIO</u> CALCULATION OF THE HELIUM-HELIUM ${}^1\Sigma_g{}^+$ POTENTIAL AT INTERMEDIATE AND LARGE SEPARATIONS*

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A five-configuration wave function computed by multiconfiguration self-consistent field techniques has yielded a well depth $\epsilon/k = 10.48$ °K at $r_m = 5.659$ bohrs and a potential zero $\sigma = 5.037$ bohrs for the interaction of ground-state He atoms. Improvement of the basis set yields, at R = 5.60, a potential U(R) = 11.38°K. It is suggested that calculations in the vein of the present approximation should converge to a well depth of close to 12° K. The long-range behavior of our potential is unexpectedly close to that commonly accepted for He-He and may change by as much as 15% as the wave function, in its present approximation, is improved.

Over the years there has been considerable interest in the interaction potential for two helium atoms as a function of internuclear distance R. The determination of this interaction potential has proceeded along two paths, semiempirical¹⁻⁷ and ab initio.⁸⁻¹³ The semiempirical potentials have been deduced by inversion of experimental scattering, second virial coefficient, and transport property data. The potentials so obtained have been useful in the elucidation of the magnitude of basic potential parameters such as well depth, ϵ , and position of the potential zero, σ . However, ambiguities are inherent in the exact form of the potential, and values of the potential parameters are not known with certainty.^{2,14} These ambiguities can be traced to experimental uncertainties coupled with the insensitivity of the experimentally measured quantities to the exact form of the potential.¹⁵

Thus theoretical calculations in which the consequences of the approximations involved are well understood and can be made arbitrarily small are of great importance in the attainment of accurate interatomic potentials. The <u>ab initio</u> short-range (0.25-3.78 bohrs) form of the He₂ potential is known quite accurately from work of Phillipson⁸ and of Matsumoto, Bender, and Davidson.⁹ Similarly, the long-range (R > 7.5 bohrs) potential is also well determined by the calculations of Dalgarno⁷ and Davison.¹¹ Only in the intermediate region around the van der Waals minimum has there been a lack of high-quality <u>ab ini-</u> tio calculations.

A series of calculations which are making progress in describing this region of interaction has been undertaken, the first of which is reported at this time.¹⁶ One of the aims of this series has been to obtain an accurate potential curve for He_2 over the entire range of internuclear distances by a single consistent computational technique and model.

The techniques we have used in this work are an extension of a scheme which has been applied successfully to obtain chemically accurate potential curves for a variety of diatomic systems (e.g., H_2 ,¹⁷ F_2 ,¹⁸ Na_2 ,¹⁹ and the long-range interaction²⁰ in HeH). In these calculations, we have used an approximation to a full multiconfiguration self-consistent field (MCSCF) method.^{17,21-23} In an MCSCF calculation, the system wave function is expanded in a linear combination of Slater determinants,

$$\Psi = \sum_{i} A_{i} \Phi_{i} \,. \tag{1}$$

Both the set of mixing coefficients, A_i , and the orbitals from which the Slater determinants are constructed are determined variationally. This latter flexibility leads to rapid convergence of the expansion wave function Ψ , in contrast to a conventional configuration-interaction calculation in which only the mixing coefficients are optimally determined.²⁴ The MCSCF wave function is, in final effect, equivalent to an expansion of the wave function in terms of natural orbitals.

In this calculation, the ground-state molecular orbitals (MO's) obtained by the Roothaan-Hartree-Fock²⁵ method at each internuclear distance were transformed to orbitals localized on each center. The basis set consisted of fourteen σ , eight π , and four δ Slater-type functions through atomic *d* functions. Calculations were performed from 5.0 to 10.0 bohrs. A single calculation was also performed at R = 5.60 with a larger basis set to which *f* functions were added. At these distances, the localization procedure yields orbitals which are quite localized on their respective centers.

The localized orbitals obtained from the Hartree-Fock MO's at each value of R were frozen in the MCSCF calculations. As a consequence of this approximation, along with the types of excitations which were allowed in the MCSCF procedure, the resulting asymptotic limit of the wave function Ψ for infinite separation, in this approximation, is that of two Hartree-Fock helium atoms.

Pair excitations were allowed which promoted one electron from each localized orbital into separate excited orbitals which were automatically localized by the MCSCF process. These sorts of excitations are of the type which contribute to the second-order perturbation energy in the perturbation treatment of long-range forces.¹⁵ The excited configurations were four in number. These four excited configurations, together with the basis set consisting of atomic functions through d's, allowed for dipole-dipole, dipolequadrupole, and most of the quadrupole-quadrupole effects which give rise to the R^{-6} , R^{-8} , and R^{-10} terms, respectively, in the perturbation expansion of the long-range potential. The five configurations important in our calculations were

$$\begin{split} \Phi_{0} &= \sigma \mathbf{1} \mathbf{s}_{A}^{2} \sigma \mathbf{1} \mathbf{s}_{B}^{2}, \\ \Phi_{1} &= \sigma \mathbf{1} \mathbf{s}_{A} \sigma \mathbf{1} \mathbf{s}_{B} \sigma_{A}' \sigma_{B}' \quad (^{1}\Sigma^{+} \times ^{1}\Sigma^{+}), \\ \Phi_{2} &= \sigma \mathbf{1} \mathbf{s}_{A} \sigma \mathbf{1} \mathbf{s}_{B} \sigma_{A}' \sigma_{B}' \quad (^{3}\Sigma^{+} \times ^{3}\Sigma^{+}), \\ \Phi_{3} &= \sigma \mathbf{1} \mathbf{s}_{A} \sigma \mathbf{1} \mathbf{s}_{B} \pi_{A} \pi_{B} \quad (^{1}\Sigma^{+} \times ^{1}\Sigma^{+}), \\ \Phi_{4} &= \sigma \mathbf{1} \mathbf{s}_{A} \sigma \mathbf{1} \mathbf{s}_{B} \pi_{A} \pi_{B} \quad (^{3}\Sigma^{+} \times ^{3}\Sigma^{+}), \end{split}$$

$$\end{split}$$

where the direct products in parentheses denote the parentage of the resultant ${}^{1}\Sigma^{+}$ state due to the different possible spin assignments among the open-shell orbital pairs, $\sigma 1s_{A}\sigma 1s_{B}$ and $\sigma_{A}'\sigma_{B}'$ or $\pi_{A}\pi_{B}$.

The σ_A' , σ_B' , π_A , and π_B orbitals resulting from the MCSCF procedure contain, because of their natural orbital character, large mixtures of both the ρ and d basis functions. It is this optimum mixture of basis functions which gives rise to the rapid convergence of the expansion.

It can easily be seen that the two configurations

 $\Phi_5 = \sigma \mathbf{1} s_A \sigma \mathbf{1} s_B \delta_A \delta_B \quad (^1\Sigma^+ \times ^1\Sigma^+)$

and

$$\Phi_{\mathbf{6}} = \sigma \mathbf{1} \mathbf{s}_{\mathbf{A}} \sigma \mathbf{1} \mathbf{s}_{\mathbf{B}} \delta_{\mathbf{A}} \delta_{\mathbf{B}} \quad (^{3} \Sigma^{+} \times ^{3} \Sigma^{+}) \tag{3}$$

are the two configurations necessary to obtain the neglected quadrupole-quadrupole contributions. When atomic f functions are added to the above basis set, the first five configurations [Eqs. (2)] yield, in addition to the above contributions, part of the dipole-octupole contribution to the R^{-10} term of the long-range potential. With the addition of the following two configurations,

$$\Phi_{7} = \sigma 1 s_{A} \sigma 1 s_{B} \varphi_{A} \varphi_{B} \quad (^{1}\Sigma^{+} \times ^{1}\Sigma^{+})$$

and

$$\Phi_{B} = \sigma \mathbf{1} s_{A} \sigma \mathbf{1} s_{B} \varphi_{A} \varphi_{B} \quad (^{3}\Sigma^{+} \times ^{3}\Sigma^{+}), \tag{4}$$

together with Eqs. (3), a total of nine configurations, our calculations contain all terms necessary to obtain the predominant contributions to the potential from the dipole-dipole through the dipole-octupole interactions. The MCSCF results are presented in the Table I and are compared with various potentials in Table II and Fig. 1. The results can be seen to agree well with accepted values for the potential parameters ϵ and σ , as well as with the long-range form of the potential.

Since our wave function tends to the atomic Hartree-Fock function for helium, and since perturbation calculations of the long-range potential using such a wave function yield values more negative¹² than those calculated with a very accu-

Table I. Helium-helium interaction.

Internuclear distance <i>R</i> (bohrs)	Total energy ^a $E(R)$ (hartrees)
5.00	-5.723 355 31
5.40	-5.72338912
5.50	-5.72339136
	$(-5.72339142)^{\mathrm{b}}$
5.60	-5.72339231
	(-5.723 395 26) ^c
	(-5.723 395 28) ^d
6.00	-5.72338917
7.00	-5.72337396
8.00	-5.72336592
9.00	-5.72336245
10.00	-5.72336090
æ	-5.723 359 24 ^e

^aOne hartree = 27.2107 eV. Unless otherwise noted the total energies listed are the five-configuration results for the basis set without atomic f functions referred to in the text. The primary configuration was constructed from frozen localized Hartree-Fock MO's.

^b The seven-configuration result at R = 5.50 for the basis set without atomic *f* functions.

^c The five-configuration result at R = 5.60 for the basis set with atomic *f* functions.

^d The nine-configuration result at R = 5.60 for the basis set with atomic *f* functions.

^e Twice the atomic Hartree-Fock energy for the helium accurate atomic basis set.

Internuclear Distance R(bohrs)	U(R) This Work (au x 10-5	U(R)/k ^f This Work) (°K)	U(R) Beck ^g (au x 10 ⁻⁵)	U(R) Murrell & Shaw ^g (au x 10 ⁻⁵)	U(R) Dalgarno ^g (au x 10 ⁻⁵)
4.00			82.05	99.86	
4.50			16.33	19.54	
5.00	.393	1.24	284	013	
5.40	-2.988	-9.435	-3.082		
5.50	-3.212	-10.14	-3.243	-3.321	
	(-3.218) ^b	(-10.16) ^b			
5.60	-3.307	-10.44	-3.294		
	(-3.602) ^C	(-11.37) ^C			
	(-3.604) ^d	(-11.38) ^d			
6.00	-2.993	-9.451	-2.903	-2.960	
7.00	-1.472	-4.648	-1.395	-1.409	-1.559
7.50			930	940	9997
8.00	662	-2.11	627		662
9.00	321		303		314
10.00	166	524	158		163
ε	-3.321 ^e	-10.48	-3.284	-3.381 ^e	
r _m (bohrs)	5.659 ^e	5.659	5.612	5.615 ^e	
σ (bohrs)	5.037 ^e	5.037	4.985	4.999 ^e	

Table II. Comparison of He-He potential curves.^a

^aSee footnote a of Table I.

^bSee Table I.

^cSee Table I.

^dSee Table I.

^eObtained by fitting an exponential spline function to the potential.

^f k is Boltzmann's constant.

^gSee Refs. 1, 13, and 7b.

rate 80-parameter wave function,¹¹ and since our potential is everywhere below the accepted long-range potential in its range of applicability, it can be seen that the improvement of the basis set with f functions and the addition of the four extra configurations, Eqs. (3) and (4), necessary to give the complete R^{-10} term will tend to shift our potential in the expected manner.

In Table I are also listed values of the potential at R = 5.50 and R = 5.60 bohrs involving seven configurations (without f functions) and nine configurations (with f functions), respectively. We see that the nine-configuration result yields a potential of 11.38°K at 5.60 bohrs. Augmentation of the basis with more functions will probably converge upon a well depth ϵ/k of close to 12°K. Such a depth has been obtained in several semiempirical potentials²; however, recent investigations of low-temperature equilibrium and transport data¹⁴ using these potentials have indicated that such well depths are probably too large and that a depth of about 10.2° K is more likely.

We have obtained good agreement with the commonly accepted potentials for He_2 . This agreement results in spite of the assumption, implicit in our asymptotic limit, that the changes in the effects of <u>intra-atomic</u> correlation energy are small at these distances and that the uncorrelated atomic-helium wave function can give an adequate description of the charge density at large separations. These two assumptions have been estimated to be good to within 10 to 15% for heli-



FIG. 1. Comparison of helium potential curves: solid line, present work; dashed line, Beck (Ref. 1); dotted line, Murrell and Shaw (Ref. 13); dot-dashed line, Dalgarno (Ref. 7b).

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In progress at present are calculations designed to evaluate the changes in the effect of intra-atomic correlation with a wave function which approaches an MCSCF atomic asymptotic limit. We feel that the model will yield a very accurate potential curve and a clearer idea of how the various terms contribute to the van der Waals region of the potential.

We further believe that the MCSCF method employed here is certainly applicable to other closed-shell interactions, and with clear changes to appropriate closed-open and open-open shell long-range forces; in fact recent success has been achieved by similar techniques for Li₂.²⁶

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