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Citation: *The Journal of Chemical Physics* **99**, 345 (1993); doi: 10.1063/1.465812

View online: <http://dx.doi.org/10.1063/1.465812>

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An exact quantum Monte Carlo calculation of the helium–helium intermolecular potential

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(Received 15 December 1992; accepted 25 March 1993)

We report “exact” *ab initio* calculations of potential energies for the interaction of two helium atoms. The quantum Monte Carlo method used is exact in that it requires no mathematical or physical approximations beyond those of the Schrödinger equation. As in most Monte Carlo methods there is a statistical or sampling error which is readily estimated. For the equilibrium internuclear distance of 5.6 bohr, the calculated electronic energy is $-5.807\,483\,6 \pm 0.000\,000\,3$ hartrees and the corresponding well depth (ϵ/k) is 11.01 ± 0.10 K. The calculated total energies are approximately 0.004 hartrees or 1200 K below the most recent variational calculations of Liu and McLean [J. Chem. Phys. **92**, 2348 (1989)]. The calculated interaction energies are in excellent agreement with the interaction energies of Liu and McLean and with a recent experimental/theoretical compromise potential energy curve of Aziz and Slaman [J. Chem. Phys. **94**, 8047 (1991)] which successfully predicts a variety of experimental measurements. The error bars of the “exact” quantum Monte Carlo interaction energies straddle the Liu–McLean and Aziz–Slaman results. The Monte Carlo results support the existence of a bound dimer state.

I. INTRODUCTION

The accurate determination of the interaction of two helium atoms, the simplest rare gas pair, has presented a difficult problem for both theory and experiment. Although early estimates of the attractive well, with a minimum in the range of -5 to -15 K relative to separated atoms, have turned out to be remarkably accurate, it has taken some sixty years of development of quantum mechanical methods to narrow the uncertainty in theoretical predictions to the vicinity of 0.1 K.

The progress of predictions may be seen in the list of theoretical studies^{1–53} in Table I, in the list of scattering experiments^{54–71} in Table II, and in the abbreviated list of model potentials^{72–79} in Table III. The recent experimental/theoretical compromise potential of Aziz and Slaman,⁷⁹ obtained by a very slight modification of the most recent *ab initio* potential of Liu and McLean,⁴⁸ is successful in predicting a variety of experimental measurements, including scattering cross sections, transport properties, and second virial coefficients.

Liu and McLean⁴⁸ have noted the problems of “wishful thinking and inadequate convergence studies” in earlier theoretical work. In their most recent work, Liu and McLean⁴⁸ used balanced treatments of molecules and separated atoms (superposition treatments) with well defined extrapolations to obtain estimates of the exact interaction energies and their uncertainties. We have no reason to doubt the accuracy estimated for their most recent potential (in fact, we confirm their results), but we do feel that one should be a little nervous about their estimated uncer-

tainty of ± 0.03 K in the interaction potential when the calculated total energy is 1200 K above the exact total energy.

We report here “exact” quantum Monte Carlo calculations of the electronic energy of two helium atoms at internuclear distances in the region of the potential well. In these the total energies are determined with accuracies previously unattained. We compare the interaction potential obtained with potentials derived from variational calculations by Liu and McLean and from others, with the Aziz–Slaman compromise potential, and with the predictions of earlier Monte Carlo calculations of several types.

II. PREVIOUS WORK

The weak attractive van der Waals forces between polar/polar and polar/nonpolar molecules were explained by Keesom⁸⁰ and Debye⁸¹ in the early 1920’s as due to dipole/dipole and dipole/induced-dipole attractions. Ten years later it was found with the help of quantum mechanics that the attraction between the fluctuating electric moment in one molecule and the induced moment in the other could lead to even greater forces. This provided an explanation of the attractive forces between noble gas atoms.

In 1927 Wang⁸² made approximate quantum calculations of the long range attraction of two hydrogen atoms and found an inverse-sixth variation of potential energy with distance. Although it was not explicitly stated, the attraction between the fluctuating electric moments and the induced moments was implicit in the calculations. In 1928 Slater¹ obtained a potential curve for the interaction

TABLE I. Theoretical treatments of the helium-helium interaction.

Reference	Date	Type	Results ^a	Reference	Date	Type	Results ^a
1	1928	HL+estimate	-8.9 K at 5.6 bohr	28	1973	MCSCF atoms+intercorrel	-10.48 K at 5.60 bohr, -10.79 K (adjusted), $E(\text{inf}) = -5.795\,308$ a.u.
2	1930	SCF very small basis	Repulsive only	29	1973	CI atoms+intercorrel	-9.5 K at 5.71 bohr $E(\text{inf}) = -5.795\,031$ a.u.
3	1931	HL+dispersion	-9.1 K at 5.8 bohr	30	1973	SCF	No well observed $E(\text{inf}) = -5.719\,98$ a.u.
4	1931	HL	Repulsion only	31	1975	SCF+perturbation	-11.25 K at 5.65 bohr
5	1939	SCF+perturbation	-13.0 K at 5.3 bohr	32	1975	CI atoms+intercorrel	-10.76 K
6	1950	SCF very small basis	Repulsive only	33	1976	SCF atoms+perturbation	-10.7 to -13.4 K at 5.6 bohr
7	1955	SCF small basis	-6.8 K at 5.9 bohr	34	1976	SCF <i>w/ghost</i> orbitals	Illustrates superposition error
8	1956	SCF	Short range	35	1977	CID <i>w/ghost</i> orbitals	-10.54 K at 5.73 bohr
9	1957	SCF	Short range	36	1977	Perturbation	Exchange dispersion energy
	1957	SCF	Short range				
	1958	SCF	Short range				
10	1958	SCF+perturbation	-8.8 K at 5.6 bohr	37	1978	Variational QMC	Preliminary results
11	1960	SCF	Well observed	38	1979	CEPA-PNO	-10.55 K at 5.63 bohr $E(\text{inf}) = -5.804\,128$ a.u. Adjusted to experiment < -11.21±0.43 K at 5.6 bohr $E(\text{inf}) = -5.807\,449$ a.u.
12	1960	SCF+perturbation	-5.3 K at 5.9 bohr	39	1980	Variational QMC	For dispersion coefficients
13	1961	SCF small basis	-8.97 K at 5.10 bohr $E(\text{inf}) = -5.695\,312$ a.u.	40	1984	SCF atoms+perturbation	
14	1962	HL+perturbation	-5.7 K at 5.0 bohr	41	1986	CEPA2	-9.55 K at 5.60 bohr
15	1962	CI 64-term	-0.33 K at 6.24 bohr $E(\text{inf}) = -5.755$ a.u.	42	1986	CEPA1	-9.29 at 5.60 bohr
16	1963	HL and MO	Short range only	43	1986	Exact QMC transient estimate	1.0-3.0 bohr $E(\text{inf}) = -5.807\,449$ a.u.
17	1966	variation+perturbation	Very long range only	44	1987	CC+perturbation	-10.64 K at 5.6 bohr
18	1966	variation+perturbation	-4.32 K at 5.75 bohr	45	1987	MP2	-6.9 K at 5.6 bohr
						MP4	-8.5 K at 5.6 bohr
19	1966	variation+perturbation	Very long range only	46	1988	MP2 and MP3	Investigating basis set effects
20	1966	CI	Short range only	47	1988	MR-CI <i>w/counterpoise</i>	-10.98 K at 5.6 bohr
21	1967	SCF atoms+perturbation	-10.49 K at 5.5 bohr	48	1989	CI atoms+intercorrel	-10.94 K at 5.61 bohr $E(\text{inf}) = -5.803\,680$ a.u.
22	1967	CI	Short range only	49	1990	MR-CI <i>w/counterpoise</i>	-10.87 K at 5.6 bohr
23	1967	SCF	no well observed $E(\text{inf}) = -5.723\,348$ a.u.	50	1990	Variational QMC fixed-node QMC	< -10.46±0.23 K < -10.2±0.6 K at 5.6 bohr $E(\text{inf}) = -5.807\,449$ a.u.
24	1968	SCF near HF limit	no well observed $E(\text{inf}) = -5.723\,395$ a.u.	51	1991	Variational QMC	< -10.60±0.24 K at 5.6 bohr $E(\text{inf}) = -5.807\,449$ a.u.
25	1970	MCSCF atoms+intercorrel	-11.38 K at 5.6 bohr $E(\text{inf}) = -5.723\,395$ a.u.	52	1991	MR-CI <i>w/counterpoise</i>	-10.92 K at 5.6 bohr
26	1970	SCF atoms+intercorrel	-12.0 K at 5.6 bohr $E(\text{inf}) = -5.732\,359$ a.u.	53	1992	MP4SDTQ	-10.04 K at 5.6 bohr $E(\text{inf}) = -5.793\,412$ a.u.
27	1971	SCF atoms+intercorrel	-12.02 K at 5.56 bohr $E(\text{inf}) = -5.732\,359$ a.u.	This work	1993	Exact QMC cancellation	-11.01±0.10 K at 5.6 bohr $E(\text{inf}) = -5.807\,449$ a.u.

^aEnergy at bottom of well relative to that for separated atoms. The notation < -*x* indicates a minimum equal to or lower than -*x*. $E(\text{inf})$ is the total energy calculated for infinite separation.

of two helium atoms by combining the repulsive forces from a Heitler-London calculation with attractive forces estimated from Wang's results for hydrogen atoms. The minimum in the curve was -8.9 K (relative to zero for separated atoms) at an internuclear distance of 5.6 bohr. These figures were in fair agreement with Slater's estimates from experimental information available in 1928 and in even better agreement with estimates from information available today.

In 1930 Eisenshitz and London⁸³ and London⁸⁴ described explicitly the nature of the fluctuating moment/induced-moment attraction and provided a simple approximate method of estimating the resulting forces between

molecules. The method was a double perturbation method. The forces became known as "London dispersion forces."

The list in Table I of theoretical predictions of the interaction of two helium atoms includes a number of double perturbation calculations from the 1930's to the 1980's. These vary in their treatment of the unperturbed atoms and of the perturbation. Until about 1970 they were more successful than other methods.

The pure self-consistent field (SCF) calculations listed in Table I show an interesting pattern. The calculations of the 1930's with very small basis sets predicted repulsion only and no attractive wells. The calculations of the 1950's with somewhat larger basis sets were successful in predict-

TABLE II. Experimental measurements of helium-helium scattering.

Reference	Date	Type	Results ^a
54	1961	Total cross section	High energy repulsion
55	1962	Total cross section	No curve
56	1965	Total cross section	High energy repulsion
57	1965	Total cross section	No curve
58	1967	Total cross section	No curve
59	1967	Total cross section	High energy repulsion
60	1968	Total cross section	No curve
61	1969	Total cross section	No curve
62	1969	Total cross section	-10 K at 5.67 ± 0.11 bohr
63	1971	Differential scattering	-16.7 ± 5.8 K at 5.5 ± 0.1 bohr
64	1972	Differential scattering	-11.0 ± 0.2 K at 5.6 bohr
65	1972	Total cross section	-10.4 K
66	1972	Total cross section	-10.3 K
67	1973	Total cross section	
68	1973	Total cross section	
69	1976	Differential scattering	-10.57 at 5.61 bohr
70	1976	Total cross section	
71	1982	Total cross section	-10.74 K at 5.62 bohr assisted by theory

^aEnergy at bottom of well relative to that for separated atoms.

ing attractive wells, such as -8.97 K by Ransil,¹³ in fair agreement with experiment. The calculations of the 1960's with much larger basis sets predicted repulsion only and no wells, even near the Hartree-Fock limit. The "spurious" wells of the pure SCF calculations of the 1950's and their fortuitous agreement with predictions from experiment were merely the result of what was later to be called "basis set superposition error."⁸⁵

The first configuration interaction (CI) calculation of the helium-helium interaction was reported in 1962 by Phillipson¹⁵ who used 64 terms and obtained a minimum

TABLE III. A sampling of potential energy curves for helium-helium based on second virial coefficients, transport data, scattering data, and theoretical predictions.

Reference	Date	Type	Results ^a
72	1938	From second virial	-10.22 K at 5.42 bohr
73	1967	From second virial	-12.53 K at 5.62 bohr
74	1968	From second virial and viscosity	-10.37 K at 5.61 bohr
75	1970	from second virial and transport data	-10.77 K at 5.71 bohr
76	1979	from second virial and transport data	-10.8 K at 5.61 bohr
77	1987	From second virial and transport data and QMC	-10.948 at 5.60 bohr
78	1990	From second virial and transport data and QMC	-10.94 at 5.61 bohr
79	1991	Fit to <i>ab initio</i>	HFD-ID -10.92 at 5.613
		Fit to <i>ab initio</i>	LM2 -10.92 at 5.613
		Adjusted	LM2M2 -10.97 at 5.612

^aEnergy at bottom of well relative to that for separated atoms.

of -0.33 K. In the next decade there followed a number of greatly improved complete CI, MCSCF, and coupled treatments of SCF and CI for atoms and CI for intermolecular correlation effects.^{20,22,25-27} Most of these predicted potential minima within 1 or 2 K of currently accepted values.

In 1973 Liu and McLean reported the first of three extensive calculations of the helium-helium interaction.^{29,30,32} They recognized the extraordinary importance of "basis set superposition error" in calculations for the helium-helium system and introduced the term to the literature of quantum mechanics in their 1973 paper. In the succession of calculations Liu and McLean repeatedly improved their procedures for eliminating basis set superposition error and the sequence of minima was -9.5 K in 1973, -10.76 K in 1975, and -10.94 K in 1989. In reporting the last result they estimated the accuracy in the energy at the minimum to be ±0.03 K.

Estimating a potential energy curve from pressure-volume-temperature (PVT) data and transport properties is not unambiguous. The sampling of potentials listed in Table III shows significant variations in these estimates. A deep well at a short internuclear distance tends to produce effects similar to those of a shallow well at a longer distance. Measurements of differential scattering and total scattering provide a different kind of data for testing model potentials. Both types of scattering measurements are sensitive to the location of the well, but total cross sections are somewhat less sensitive to the well depth. An accurate potential would predict the complete variety of experimental measurements.

In 1982 the total cross-section measurements of Feltgen *et al.*⁷¹ indicated a well of -10.74 K at 5.62 bohr, intermediate between the predictions from two sets of measurements of differential cross sections by Lee and co-workers,^{64,69} matching the well of -10.8 K at 5.61 bohr found by Aziz *et al.*⁷⁶ from second virial and transport properties, and in good agreement with the well of -10.76 K at 5.62 bohr from the 1975 calculation of Liu and McLean.³² The matter of the helium-helium interaction appeared to be resolved.

However, a Monte Carlo variational calculation by Lowther and Coldwell³⁹ in 1980 gave an upper bound, with error bars, corresponding to a deeper well. They predicted a minimum equal to or deeper than -11.23 ± 0.46 K at 5.60 bohr. In 1986 Ceperley and Partridge⁴³ reported transient-estimate "exact" quantum Monte Carlo calculations for internuclear distances of 1.0-3.0 bohr giving potential energies substantially higher than the 1979 experiment-based curve of Aziz *et al.*⁷⁹ in that region. In 1987 Aziz, McCourt, and Wong⁷⁷ reported a revised potential consistent with the higher values for short distances. The revised curve had a minimum of -10.948 K at 5.60 bohr.

In their most recent calculations of 1989 Liu and McLean⁴⁸ obtained a potential (called LM-2) with a minimum of -10.94 at 5.61 bohr. Another recent set of extensive variational calculations is that by van Lenthe *et al.*⁴⁷ in 1988 giving a potential (called VVVV) with a well of -10.98 K at 5.6 bohr. Still more recent are a

calculated potential by Vos *et al.*⁴⁹ in 1990 with a minimum of -10.87 K at 5.6 bohr and a calculated potential (called VVVVR) by Vos *et al.*⁵² with a minimum of -10.92 K at 5.6 bohr.

Liu and McLean⁴⁸ have expressed doubts about adjustments to eliminate basis set superposition error in the calculations by van Lenthe *et al.*⁴⁷ Vos *et al.*⁴⁹ have expressed similar doubts about basis set superposition error in the calculations of Liu and McLean.⁴⁸

Aziz and Slaman⁷⁹ have fit analytic expressions to the LM-2 and to the VVVVR data and examined the properties of helium calculated for these potentials. Both potentials fail to predict the very low temperature ^4He and ^3He virial coefficients. Aziz and Slaman modified the LM-2 potential to give a well of -10.97 K at 5.61 bohr and found satisfactory predictions. This compromise potential predicts a variety of experimental results and is consistent with the LM-2 potential.

We note two additional Monte Carlo variational calculations^{50,51} and one fixed-node quantum Monte Carlo calculation⁵¹ giving upper bounds (with error bars) to the minimum at 5.6 bohr. These indicate a well deeper than -10.5 ± 0.1 K.

III. EXACT QUANTUM MONTE CARLO METHOD

The method used is an exact quantum Monte Carlo method which we have described in detail previously.^{86,87} It is a Green's function Monte Carlo method⁸⁸ incorporating many of the best features of earlier fixed node,⁸⁹ released node,⁹⁰ and cancellation schemes⁹¹ for incorporating the correct properties of symmetry and antisymmetry of the wave function. The method is exact in that it requires no mathematical or physical approximations beyond those of the Schrödinger equation itself. As in most Monte Carlo calculations there is a statistical or sampling error which is readily estimated. Within sampling error the wave function and the nodes of the wave function are determined exactly in the course of a calculation.

The Green's function quantum Monte Carlo method provides solutions to the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\mathbf{X}) + V(\mathbf{X})\Psi(\mathbf{X}) = E\Psi(\mathbf{X}), \quad (1)$$

in the form of samples of the exact wave function $\Psi(\mathbf{X})$. Sampling is based on the property of the Green's function which relates the wave function to itself

$$\Psi(\mathbf{X}) = \int d\mathbf{X}' G_0(\mathbf{X}, \mathbf{X}') \frac{V(\mathbf{X}')}{E} \Psi(\mathbf{X}'). \quad (2)$$

Repeated application of Eq. (2) to an initially arbitrary wave function $\Psi(\mathbf{X}')$ leads to a wave function $\Psi(\mathbf{X})$ which is the lowest-energy solution to the Schrödinger equation for the specified boundary conditions or other constraints.

The Green's function $G_0(\mathbf{X}, \mathbf{X}')$ of Eq. (2) is given by

$$G_0(\mathbf{X}, \mathbf{X}') = (2\pi)^{-3N/2} (k|\mathbf{X} - \mathbf{X}'|)^{1-3N/2} \times K_{3N/2-1}(k|\mathbf{X} - \mathbf{X}'|), \quad (3)$$

where K_ν is the modified Bessel function of the second kind.

The treatment of many electron systems and other systems with nodes is based on the partial cancellation of positive and negative wave function samples (called psi particles, psips, walkers, and many other names) having overlapping Green's functions. The theoretical basis for cancellation is described in Refs. 86 and 91. In the absence of cancellation, the wave function would be given by the small difference between large populations of positive and negative psips. With cancellation and with one or another of several schemes to enforce anti-symmetry for permutation of electrons of the same spin stable populations of mostly positive and/or mostly negative psips are maintained.⁹²

Energy determination is made with the aid of the importance sampling method of Grimm and Storer⁹³ using a trial wave function Ψ_T having the same symmetry properties as the desired wave function. The exact energy is given by

$$E = \frac{\int d\mathbf{X} \Psi \Psi_T (\hat{H} \Psi_T / \Psi_T)}{\int d\mathbf{X} \Psi \Psi_T}, \quad (4)$$

where $(\hat{H} \Psi_T / \Psi_T)$ is the local energy for the trial function. When Ψ is exact the energy is given exactly for any Ψ_T having the correct symmetry properties.

The estimate of the energy obtained from Monte Carlo sampling is given by

$$E = \frac{\sum s_i w_i \Psi_{T_i} (\hat{H} \Psi_T / \Psi_T)_i}{\sum s_i w_i \Psi_{T_i}}, \quad (5)$$

where s_i is the sign of a psip (Ψ based) and w_i is its weight. The uncertainty in energy thus determined depends on the accuracy of the trial function and the number of samples as well as any correlations of the samples. It is directly proportional to the standard deviation σ_i in local energy and inversely proportional to the square root of the number of samples. An accurate trial function and a large number of independent samples are desired.

The energies obtained are independent of the importance sampling function (with the proper symmetry) except as it affects the uncertainties in the energies. Thus, there is no basis set superposition error in our calculations.

IV. IMPORTANCE SAMPLING FUNCTION

The importance sampling function used to assist in the determination of energies was that devised by Lowther and Coldwell³⁹ for their Monte Carlo variational calculations. The function is given by

$$\begin{aligned} \Psi_T = & \phi_{A13} \phi_{B24} \exp(-\tfrac{1}{2} U_{1324}) - \phi_{A14} \phi_{B23} \\ & \times \exp(-\tfrac{1}{2} U_{1423}) - \phi_{A23} \phi_{B14} \exp(-\tfrac{1}{2} U_{2314}) \\ & + \phi_{A24} \phi_{B13} \exp(-\tfrac{1}{2} U_{2413}), \end{aligned} \quad (6)$$

where electrons 1 and 2 are spin up, electrons 3 and 4 are spin down, ϕ_{A13} is an atomic wave function for electrons 1 and 3 interacting with nucleus A, ϕ_{B24} is an atomic wave

function for electrons 2 and 4 interacting with nucleus B , U_{1324} is a cross term accounting for interactions of 1 and 3 near A with 2 and 4 near B , and so forth.

The function ϕ_{A13} (and the others like it) is Schwartz's⁹⁴ 189-term Hylleraas-type wave function for a helium atom which yields in variational calculations an energy of $-2.903\,724\,376$ hartrees, a value within about 10^{-9} hartrees of the exact value for a helium atom. The function U_{1324} (and others like it) is a sum of five complex terms containing 29 adjustable parameters optimized by Lowther and Coldwell by minimizing the variance in the local energy for each of seven internuclear distances.

The Lowther-Coldwell variational calculations³⁹ for helium atoms separated by more than 4.5 bohr produced expectation values for the energies easily within 1.0 K of the exact values for the total electronic energies. The standard deviation in local energies for our calculations (based on $\Psi\Psi_T$ samples) was about 0.0006 hartrees for a separation of 5.6 bohr. We did not optimize the trial wave functions for internuclear distances not listed by Lowther and Coldwell. For those we used the coefficients for nearby distances and standard deviations were higher.

Our analytic expressions and programs for the evaluation of the derivatives of Ψ_T and the local energies were checked by comparisons with results from numerical differentiation and by direct comparisons with the programs of Lowther and Coldwell.

V. CALCULATION PROCEDURE

The calculations were carried out as described in Refs. 86 and 87 with several minor changes in procedure to take advantage of the lower cancellation requirement required for the helium-helium system and the availability of a massively parallel computer. The nuclei were placed on the z axis. Exchange symmetry for electrons of the same spin was imposed by permuting electrons 1 and 2 for $z_2 < z_1$ and permuting electrons 3 and 4 for $z_4 < z_3$ and changing the sign of a psip with each permutation. This also had the effect of concentrating psips in a single region of configuration space.

The zero of potential energy was adjusted to give electronic energies, exclusive of the internuclear repulsion energy, of about -6.5 hartrees. This gave reasonably large step sizes for the electrons and was sufficiently negative to produce only infrequent sign changes due to positive values of $V(X')$ in Eq. (2). Sign changes from permutation of electrons were also infrequent because of the large internuclear separations investigated. As a result a stable population of psips with a large ratio of positive to negative psips was easily maintained. The total population was typically 20 000 psips.

Cancellations were carried out only for pairs of positive and negative psips each having r_{1A} , r_{3A} , r_{2B} , and r_{4B} less than 1 bohr. Psips eligible for cancellation were additionally concentrated in configuration space by rotation of all electrons about the z -axis to place electron 1 in the $y=0$ plane and by reflection in the $y=0$ plane to place electron 2 in the region $y>0$. Each eligible negative psip was paired for cancellation with the nearest eligible positive psip not

TABLE IV. Total electronic energies for the helium-helium system calculated by "exact" quantum Monte Carlo method.

Internuclear distance R (bohr)	Total electronic energy V (hartree)
3.0	$-5.795\,37 \pm 0.000\,30$
4.5	$-5.807\,259 \pm 0.000\,006$
5.0	$-5.807\,450\,0 \pm 0.000\,002\,5$
5.6	$-5.807\,483\,60 \pm 0.000\,000\,32$
6.6	$-5.807\,468\,55 \pm 0.000\,000\,32$
7.5	$-5.807\,458\,42 \pm 0.000\,000\,32$
9.0	$-5.807\,451\,81 \pm 0.000\,000\,32$
15.0	$-5.807\,448\,87 \pm 0.000\,000\,16$
infinite	$-5.807\,448\,71 \pm 0.000\,000\,06$

yet paired. It was unnecessary to use either multiple cancellations or self-cancellations to achieve higher stability.

The calculations were carried out on Thinking Machines Corporation CM-5 Connection Machine[®] computers (Connection Machine is a registered trademark of Thinking Machines Corporation), ranging in size from 32 to 256 processing nodes. The speed and memory of the processors was sufficiently high that completely independent calculations could be carried out on each processor. The code was written in in FORTRAN77 and the inclusion of calls to the message-passing library for the CM-5, CMMD, for passing a different random number seed on each node at the beginning of a run and for gathering statistics from each node at the end of a run. The CMMD library provides the routines needed to program the CM-5 in a MIMD (multiple instruction multiple data) style. This implementation required minimal changes to the existing serial code.

The statistical uncertainties in the calculated energies were determined from analyses of the variances in energies for independent blocks of calculations according to $\sigma_m = \sigma_b / \sqrt{(N_b - 1)}$, where σ_m is the standard deviation of the calculated mean, σ_b is the standard deviation of the block energies, and N_b is the number of blocks.

VI. RESULTS

Energies were determined for eight internuclear distances in the range of 3.0 to 15.0 bohr as well as for a pair of separated atoms. Results are listed in Table IV.

The potential energies relative to the exact value for a pair of separated atoms are listed in Table V and plotted in Fig. 1. Also listed in Table V are the most recent values reported by Liu and McLean⁴⁸ and the experimental/theoretical compromise potential of Aziz and Slaman⁷⁹ which is consistent with the Liu-McLean values and which predicts a number of experimental measurements. The solid curve of Fig. 1 is the Aziz-Slaman compromise potential.

VII. CALCULATED BINDING ENERGY

The existence of a stable bound state of the helium dimer has been demonstrated recently in experiments by Luo *et al.*⁹⁵ They observed the helium dimer ion after electron-impact ionization of a molecular beam formed by

TABLE V. Intermolecular potential for the helium-helium system calculated by "exact" quantum Monte Carlo method. Other values are listed for comparison.

Internuclear distance R (bohr)	Potential energy (K)		
	Exact QMC this work	Expt./Theory Aziz-Slaman ^a	Theory LM-2 Liu-McLean ^b
3.0	3812.0 \pm 96.0	3792.0	3767.0
4.5	60.0 \pm 1.9	58.5	
5.0	-0.41 \pm 0.78	-0.39	-0.33
5.6	-11.01 \pm 0.10	-10.97	-10.94
6.6	-6.25 \pm 0.10	-6.36	
7.5	-3.05 \pm 0.10	-3.06	-3.057
9.0	-0.96 \pm 0.10	-0.99	-0.985
15.0	-0.04 \pm 0.05	-0.042	
infinity	+0.01 \pm 0.02	(0.0)	(0.0)

^aReference 79.

^bReference 48.

supersonic expansion of helium and eliminated the possibility of production of the dimer ion other than by ionization of the neutral dimer species.

We have calculated the one and only stable dimer state ($v=0, j=0$) for the LM2M2 potential, which is consistent with our data. Our numerical solution for the helium masses of 7296.30 a.u. yields an energy of -0.0013 K relative to zero for separated atoms. For this energy the inner classical turning point is at 4.992 bohr and the outer is 26.6 bohr. The maximum in the wave function occurs at 7.1 bohr, the most probable internuclear distance is 13.1 bohr, and the average internuclear distance is 98.0 bohr.

The binding energy is highly sensitive to the potential energy curve and the question of a bound state is an old one,⁹⁶ but most recent calculations such as those of Uang and Stwalley⁹⁷ for a potential with a well of -10.8 K have supported the existence of a bound state.

VIII. DISCUSSION

Our calculated values of the total energies for the helium-helium system are the most accurate to date. The

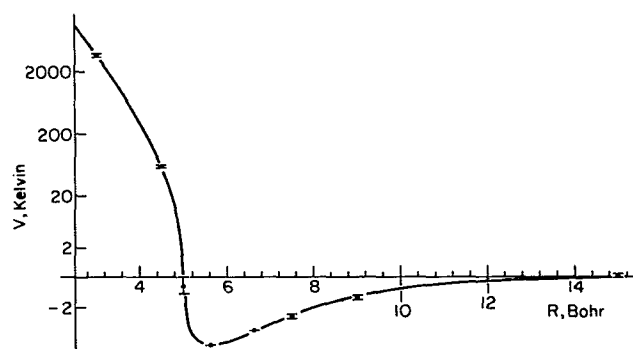


FIG. 1. Helium dimer interatomic potential: Potential energy (in degrees Kelvin) vs interatomic distance (atomic units) for the helium dimer. The gray curve is the Aziz-Slaman experimental/theoretical compromise potential (Ref. 79). The points with error bars are from this computation. The scaling of the ordinate values was done with the function $f(V) = \text{sign}(V) \ln(1 + |V|)$.

energies lie 4000 K below those of the first Liu-McLean calculations,²⁹ 1200 K below those of the most recent Liu-McLean calculations,⁴⁸ and 4400 K below those of the 1992 MP4 calculations of Tao and Pan.⁵³

Our energy calculated for the separated pair of atoms is within 0.02 K of the exact value. Our energy for a separation of 3.0 bohr is in good agreement with that by Ceperley and Partridge.⁴³ Our energies are also consistent (i.e., with appropriate consideration of error bars, below the upper limits of their values) with the Monte Carlo variational calculations of Lowther and Coldwell.³⁹

Our helium-helium interaction energies (i.e., energies relative to separated atoms) are in excellent agreement with the LM-2 values of Liu and McLean,⁴⁸ with the VVVVR values of Vos *et al.*,⁵² and with the compromise potential of Aziz and Slaman.⁷⁹ The error bars for our energies straddle the three sets of data.

There are, of course, error bars for the Liu-McLean, the Vos *et al.*, and the Aziz-Slaman results. For 5.6 bohr Liu and McLean report an uncertainty of ± 0.03 K. As we noted earlier, one should perhaps be a little nervous about ± 0.03 K relative error in calculations with a total error of 1200 K. Vos *et al.*⁵² have examined the Liu-McLean calculations and concluded "that a theoretical justification for this LM-2 potential, as well as the error bars on it, is lacking." Liu and McLean⁴⁸ have examined the Vos *et al.*⁴⁷ calculations and the contention that their adjustment of fragment energies is quantitative and "see no reason why it should be."

Since our energies straddle the LM-2 and VVVVR energies as well as the Aziz-Slaman curve, we are not in a position to claim better results. We can, however, claim the absence of basis set superposition error, any other systematic error, and any experimental inputs beyond basic constants. We feel the uncertainties in our potential energies of interaction are lower than realistic estimates of the uncertainties for the other potentials.

Another interpretation is that all four potentials really agree with each other remarkably well, easily within 0.2 K at 5.6 bohr, and each one confirms the accuracy of the others. From that point of view they are all a great success, possibly because they are all very accurate.

Should more accurate values be useful they might be obtained with additional computations using our Monte Carlo programs without improvements. As costs of computation fall at the rate of about ten every four years, the uncertainty in energy for a given computation cost falls at the rate of about ten every eight years.

ACKNOWLEDGMENTS

Acknowledgment is made to the National Science Foundation (Grant No. CHE-8714613) and to the Office of Naval Research (Grant No. N00014-92-J-1340) for support of this work.

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