

Exact quantum Monte Carlo calculation of the H-He interaction potential

Aniket Bhattacharya and James B. Anderson

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

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An exact quantum Monte Carlo method is used to calculate the H-He interaction potential under the Born-Oppenheimer approximation. The method used is exact in that it requires no mathematical or physical approximations beyond the Schrödinger equation. As in most Monte Carlo methods there is a statistical error which is readily estimated. For the equilibrium internuclear distance of 7.0 bohr the calculated electronic energy is $-3.403\,7459 \pm 0.000\,0016$ hartrees and the corresponding well depth (ϵ/k) is 6.8 ± 0.5 K. The calculated potential is consistent with low-energy scattering cross-section measurements [J. P. Toennies, W. Welz, and G. Wolf, *Chem. Phys. Lett.* **44**, 5 (1976)] and with low-temperature diffusion measurements [Hardy *et al.*, *Phys. Rev. Lett.* **45**, 453 (1980)].

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I. INTRODUCTION

The weak van der Waals attraction in the H-He system is one of the weakest of all for pairs of neutral atoms. The depth of the well in the potential-energy curve is smaller than that of the He-He system (depth $\epsilon/k = 11.0$ K at an internuclear distance R_m of 5.6 bohr [1]) and close to that for the H-H ($b^3\Sigma_u^+$) system (6.46 K at 7.8 bohr) [2].

Information on the H-He interaction potential is available from only a few experiments. High-energy scattering experiments [3–6] have given total cross sections and information about the repulsive part of the potential-energy curve. The most precise of these experiments is that by Gengenbach, Hahn, and Toennies [6]. Low-energy scattering experiments have given total cross sections and the attractive part of the potential. The only such measurements available are by Toennies, Welz, and Wolf [7]. They observed an atomic Ramsauer-Townsend effect for both H-He and D-He, from which they estimated the depth of the well. Additional experimental information is available from measurements of the diffusion coefficient of H in He gas at very low temperatures by Hardy *et al.* [8]. The low-temperature scattering data of Toennies, Welz, and Wolf were interpreted by a potential with a well depth of $\epsilon/k = 5.3$ K at $R_m = 7.0$ bohr. Later, Jochemsen, Berlinsky, and Hardy [9] showed that the scattering data as well as the low-temperature diffusion measurements were consistent with three similar potentials (empirical, semiempirical, and *ab initio*) having well depths of $\epsilon/k = 6.79$ to 7.16 K.

Our interest in the H-He interaction has been stimulated by recent studies of H atom sticking to He surfaces [10]. Sticking is expected to be strongly dependent on the interaction potential.

We report here quantum Monte Carlo calculations for the clamped nucleus, nonrelativistic H-He system which yield an interaction potential of high accuracy. The calculations are “exact” in that there are no mathematical or physical approximations beyond those of the Schrödinger equation; but, as in most Monte Carlo calcu-

lations, there are statistical errors which are easily estimated. The method was recently applied to the determination of a potential-energy curve for the He-He system [1] which was found to be consistent with the best analytical-variational treatments and with a variety of experimental measurements. In the succeeding sections we describe the calculation method, present the results for H-He, and compare them with available experimental measurements and prior theoretical predictions.

II. PREVIOUS CALCULATIONS

Theoretical treatments of the H-He system closely parallel the more numerous treatments of the He-He system. As for the He-He system, the very high accuracy required and the extreme importance of basis set superposition errors render the calculations very difficult. A summary for the H-He system is given in Table I [11–25]. The list begins with a very simple self-consistent-field (SCF) calculation by Gentile [11] in 1930 which predicted repulsion between the atoms. The addition of an attractive dispersion energy term to the energy from a two-term configuration-interaction (CI) calculation by Mason, Ross, and Shatz [12] in 1956 results in the first prediction of an attractive well. In the 1960's several different SCF and CI calculations were made with larger basis sets, but they gave no indication of an attractive well.

In the 1970s somewhat larger CI and multiconfiguration self-consistent-field (MCSCF) calculations produced the first fully *ab initio* predictions of the well. Five sets of calculations gave successively more accurate predictions. The last is that by Das, Wagner, and Wahl [22] yielding a well depth of 6.5 K at an internuclear distance of 6.8 bohr.

More recent theoretical work includes a simple model incorporating dispersion by Gayet, McCarroll, and Valiron [23] and a Hartree-Fock dispersion treatment by Scoles [25] giving a remarkably accurate prediction of a depth of 7.2 K at 6.7 bohr. An electron-gas model by Brual and Rothstein [24] is also remarkably accurate with a prediction of a depth of 6.4 K at 6.9 bohr.

TABLE I. Theoretical treatments of the H-He interaction potential.

Authors	Year	Method	Results
Gentile	1930	SCF very small basis	repulsive only
Mason, Ross, and Shatz	1956	CI 2 terms + dispersion	-2.57 K at 7.65 bohr $E(\infty) = -3.347$ hartrees
Michels and Harris	1963	CI	1-4 bohr, repulsive $E(\infty) = -3.375$ hartrees
Taylor and Harris	1964	CI	1-8 bohr, repulsive $E(\infty) = -3.392$ hartrees
Barua and Chatterjee	1964	SCF	1-3 bohr, repulsive $E(\infty) = -3.347$ hartrees
Bender and Davidson	1966	CI 31 terms	3 bohr only $E(\infty) = -3.4008$ hartrees
Fischer and Kemmey	1970	SCF	1-5 bohr, repulsive $E(\infty) = -3.362$ hartrees
Miller and Schaefer	1970	CI 321 terms	-36 K at $R = 7$ bohr $E(\infty) = -3.393268$ hartrees
Das and Ray	1970	CI 5 terms	-3.4 K at $R = 7.0$ bohr
Das and Wahl	1971	MCSCF 7 terms	-5.3 K at $R = 7$ bohr $E(\infty) = -3.361672$ hartrees
Davison and Liew	1972	CI 19 terms GVB	-11.1 K at $R = 6.8$ bohr $E(\infty) = -3.37676$ hartrees
Das, Wagner, and Wahl	1978	MCSCF 7 terms	-6.5 K at $R = 6.8$ bohr $E(\infty) = -3.361673$ hartrees
Gayet, McCarrol, and Valiron	1978	model + dispersion	-4.2 K at $R = 7.1$ bohr -4.9 K at 6.9 bohr
Brual and Rothstein	1979	electron gas model	-6.4 K at $r = 6.8$ bohr
Scoles	1984	HR + dispersion semiempirical	-7.2 K at $R = 6.7$ bohr
Present work	1993	QMC	-6.8±0.5 K at $R = 7.0$ bohr $E(\infty) = -3.4037243$ hartrees

III. METHOD

In this work we have used the Green's-function Monte Carlo method with an efficient cancellation scheme proposed by Anderson, Traynor, and Boghosian [26]. It is based on a cancellation scheme first proposed by Arnou *et al.* [27]. Here we describe it briefly. First one recasts the Schrödinger equation in its integral form given by

$$\Psi(\mathbf{X}) = \int d\mathbf{X}' G_0(\mathbf{X}, \mathbf{X}') \frac{V(\mathbf{X}')}{E} \Psi(\mathbf{X}'), \quad (1)$$

where $\mathbf{X}[\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_{3N}]$ is the $3N$ -dimensional vector, and V contains the interelectron and the electron-nuclear potential. The form of the Green's function $G_0(\mathbf{X}, \mathbf{X}')$ is known exactly [28] and is given by

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

where $K_\nu(|\mathbf{X} - \mathbf{X}'|)$ is the Bessel function of imaginary argument. In particular, for the case of three electrons the above expression reduces to

$$G(|\mathbf{R}|) = \left[\frac{2\pi}{R} \right]^{1/2} \left[\frac{15}{R^3} + \frac{15}{R^2} + \frac{6}{R} \right] \exp(-R). \quad (3)$$

One starts with a collection of representative particle wave-function samples [PSIPS (psi particles)], usually drawn from a good trial wave function, and samples the move by the Green's function. In order to get a large positive-to-negative ratio of the PSIPS a cancellation scheme is used in which the weight of a particular PSIP may be wholly or partially cancelled by a nearby PSIP with opposite sign. By cancelling the positive and negative PSIPS according to their weights, it is possible to maintain a steady large ratio of positive-to-negative PSIPS. The energy is evaluated with the use of importance sampling, according to the formula

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

TABLE II. Optimized parameters of trial wave function for $R_{AB} = 7.0$ bohr.

b_{1B}	-0.060 79	c_{1B}	0.194 48
b_{2B}	-1.000 00	c_{2B}	0.000 01
b_{3B}	-0.041 07	c_{3B}	0.134 72
b_{2A}	-0.144 06	c_{2A}	0.223 71
b_{12}	0.112 50	c_{12}	0.315 89
b_{32}	0.166 74	c_{32}	0.414 20

TABLE III. Calculated H-He interaction energies.

r_{AB} (in bohr)	Present work (in hartrees)
5.0	-3.403 5064±0.000 0142
5.5	-3.403 6734±0.000 0050
6.0	-3.403 7386±0.000 0030
6.5	-3.403 7445±0.000 0015
7.0	-3.403 7459±0.000 0016
7.5	-3.403 7399±0.000 0015
8.0	-3.403 7382±0.000 0006
9.0	-3.403 7306±0.000 0006
10.0	-3.403 7276±0.000 0007
11.0	-3.403 7250±0.000 0006
15.0	-3.403 7246±0.000 0003
∞	-3.403 7243±0.000 0001

and the Monte Carlo estimate of the energy is given by

$$E = \frac{\sum_i s_i w_i \Psi_{Ti} \left[\frac{H\Psi_T}{\Psi_T} \right]_i}{\sum_i s_i w_i \Psi_{Ti}}, \quad (5)$$

where s_i and w_i are the sign and the weight of the PSIP with an approximate or trial wave function Ψ_{Ti} .

The trial wave function is constructed as an antisymmetrized product of a $1s$ wave function for hydrogen and a Hylleraas $1s^2$ wave function [29] for helium,

$$\Psi = [\psi_A(1,3)\psi_B(2)\psi_J(1,3,2) - \psi_A(2,3)\psi_B(1)\psi_J(2,3,1)], \quad (6)$$

where the two spin-up electrons are denoted 1 and 2 and the spin-down electron is denoted 3. The helium and the hydrogen nuclei are denoted A and B , respectively. The term $\psi_A(1,3)$ is a Hylleraas wave function containing 189 terms due to Schwartz [30] given by

$$\psi_A(1,3) = \exp(-ks/2) \sum_{l,m,n} C_{lmn} s^l t^m u^n, \quad (7)$$

where $s = r_{1A} + r_{3A}$, $t = r_{1A} - r_{3A}$, $u = r_{13}$, and $k = 3.5$

with $l = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$, etc., $m = 0, 1, 2, \dots$, etc., $n = 0, 2, 4, \dots$, etc.

The term $\psi_B(2)$ contains the hydrogen orbital for electron 2 centered at B and the term ψ_J contains Jastrow terms for electron-electron and electron-nucleus correlations. These terms are given by

$$\psi_B(2) = \exp \left[\frac{b_{2B} r_{2B}}{1 + c_{2B} r_{2B}} \right] \quad (8)$$

and

$$\psi_J(1,3,2) = \exp \left[\frac{b_{1B} r_{1B}}{1 + c_{1B} r_{1B}} + \frac{b_{3B} r_{3B}}{1 + c_{3B} r_{3B}} + \frac{b_{2A} r_{2A}}{1 + c_{2A} r_{2A}} + \frac{b_{12} r_{12}}{1 + c_{12} r_{12}} + \frac{b_{32} r_{32}}{1 + c_{32} r_{32}} \right]. \quad (9)$$

The expressions for $\psi_A(2,3)$, $\psi_B(1)$, and $\psi_J(2,3,1)$ are obtained by interchanging 1 with 2 in the above expressions. The coefficients b_{ij} and c_{ij} were optimized to obtain the minimum variance in local energies [31]. The optimized coefficients for $r_{AB} = 7.0$ are listed in Table II.

In our present calculation the ratio of positive PSIPS to negative PSIPS was very high (about 100 to 1). The preliminary testing and development of the code was done with an IBM RS/6000 machine. Production runs were carried out with a Cray C-90 using a code adapted to the vector capabilities of the machine to obtain speeds of about 350 megaflops. One can calculate the trial wave function and its derivatives for many PSIPS independently of each other. Since this part of the calculation, especially with a Hylleraas wave function, is a major part of the program, it makes a significant difference in running the code on a vector machine like the C-90.

IV. RESULTS

Energies were determined for eleven internuclear distances as well as for completely separated atoms. Results

TABLE IV. Comparison of H-He potential energies from several sources.

r_{AB} (in bohr)	Present work (in K)	R2 (Ref. 9) (in K)	HFD-B (Ref. 9) (in K)	DWW (Ref. 22) (in K)
5.0	68.8±4.45	89.2	82.1	94.0
5.5	16.10±1.56	26.9	18.0	
6.0	-4.48±0.94	1.45	-2.27	-0.3
6.5	-6.36±0.46	-6.34	-6.94	-6.0
7.0	-6.80±0.53	-6.76	-6.68	-6.6
7.5	-4.90±0.49	-5.55	-5.27	-5.4
8.0	-4.36±0.20	-4.23	-3.87	-4.1
9.0	-1.95±0.20	-2.06	-1.98	-1.9
10.0	-1.03±0.23	-1.05	-1.04	
11.0	-0.20±0.20	-0.57	-0.58	
15.0	-0.06±0.10	-0.08	-0.08	
∞	-0.02±0.02			

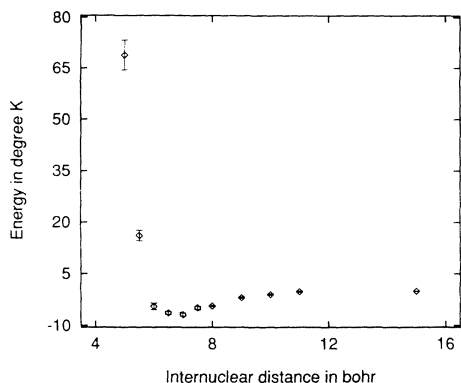


FIG. 1. Calculated interaction potential as a function of internuclear distance.

are listed in Table III. Error bars are estimated from the variances in the calculated energies for repeated calculations.

The potential energies relative to the exact value for separated atoms are listed in Table III and plotted in Fig. 1. Also listed in Table IV are values for three potential curves found by Jochemsen, Berlinsky, and Hardy [9] to be consistent with scattering and diffusion measurements.

V. DISCUSSION

Since Jochemsen, Berlinsky, and Hardy [9] made a careful analysis of the scattering and diffusion phenomena and predicted for several potential-energy curves, it is convenient to discuss our results in terms of theirs. Jochemsen, Berlinsky, and Hardy found that three potential-energy curves gave excellent predictions of the experimental observations of Toennies, Welz, and Wolf [7] and Hardy *et al.* [8]. The three potentials are the following: R2, an empirical potential formulated by Jochemsen, Berlinsky, and Hardy (Fig 2) [9] to fit the observed data; HFD-B, a semiempirical potential resulting from a Hartree-Fock dispersion calculation by Scoles [9]; and DWW, the *ab initio* potential from the MCSCF calculations of Das, Wagner, and Wahl [22]. Values for these three potentials are listed in Table IV along with

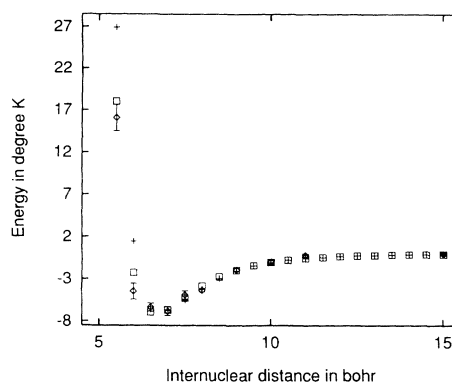


FIG. 2. Comparison of present results (diamonds with error bars) with empirical potentials due to Jochemsen, Berlinsky, and Hardy (plus signs) and due to Scoles (squares with dots).

our present results.

The R2, HFD-B, and DWW curves are in good agreement with each other and with our quantum Monte Carlo results. The differences in energies are less than one or two of our standard deviations except at the smallest internuclear distances. Thus, our calculated potential is, in turn, consistent with the low-energy measurements of Toennies, Welz, and Wolf [7] and the low-temperature diffusion measurements of Hardy *et al.* [8]. We note that the lowest total energy obtained in analytic variational calculations that by Das, Wagner, and Wahl [22] is 0.042 hartree, or 12 000 K above the exact total energy. The quantum Monte Carlo energy is 12 000 K lower, but the well depths from the two calculations are within 1 K of each other.

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