The interaction potential of a symmetric helium trimer

Aniket Bhattacharya and James B. Anderson
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

The interaction potential of three helium atoms in symmetric linear configurations is calculated under the Born–Oppenheimer approximation using an "exact" Green's function quantum Monte Carlo method. The results are compared with those of "exact" quantum Monte Carlo calculations for the helium dimer and the Axilrod–Teller triple-dipole energy expression. For nearest neighbor separations of 5.6 bohrs, the equilibrium distance for a helium dimer, the corresponding trimer energy is -21.5 ± 1.9 K, compared to -22.3 ± 0.2 K, calculated for pairwise additive behavior. For all internuclear separations in the neighborhood of the van der Waals well ($\sim$5.6 bohrs), the nonadditive contribution is found to be very small.

The interaction between two helium atoms has recently been calculated accurately by analytic variational[1,2] as well as "exact" Green's function Monte Carlo methods.[3] The calculated potentials are in good agreement with an experimental–theoretical compromise potential[4] which is consistent with many experimental measurements. For distances close to the van der Waals minimum for the three helium atoms, the interaction is generally expected to be very nearly equal to the sum of the interaction of the three pairs of atoms. The higher order terms are believed to be extremely small and are usually referred to as the "nonadditive" contribution to the total energy. In this paper, we present "exact" results for the interaction potential of a helium trimer in symmetric linear configuration.

Calculations for helium trimers began in the 1940s. The first set of perturbative calculations were due to Axilrod and Teller[5] and Muto.[6] Their expression for the triple–dipole interaction energy calculated from a third-order perturbation expansion is given by

$$\Delta E^3 = C \, \frac{3 \cos \gamma_1 \cos \gamma_2 \cos \gamma_3 + 1}{r_{12}^3 r_{23}^3 r_{31}^3}, \qquad (1)$$

where r_{12}, r_{23}, and r_{31} are the internuclear distances and γ_1, γ_2, and γ_3 are the angles included by the corresponding sides. The constant C is independent of the geometry and is directly proportional to the polarizability.[7] We refer to this expression as the Axilrod–Teller form. For a linear trimer, the expression yields an attractive contribution to the energy, while for a right-angled or an equilateral triangle trimer, the contribution is repulsive. Midzuno and Kihara[7] derived a similar expression for spherically symmetric atoms. It has been argued[8] that the above expression is the only important contribution even for dense inert gases. Rosen[9] calculated the repulsive part of the interaction by the valence bond method. Shostak[10] used Roothaan's self-consistent LCAO method to calculate the interaction energy of a linear arrangement of three helium atoms. Sherwood, De Rocco, and Mason[11] estimated the effect of nonadditive three-body forces on the third virial coefficient. Novaro and Beltran-Lopez[12] predicted the potential energy surface of He_3 with self-consistent-field linear-combination-of-atomic-orbitals molecular-orbital (SCF-LCAO-MO) calculations to test the pairwise additivity at short ranges. Based on their calculations

they have raised interesting issues of how the three-body and four-body correlations, although small, can affect the convergence of many-body expansions. The many-body contributions to interaction potentials and the nonadditivity of the second-order exchange-dispersion energy have also been addressed in terms of very large basis set *ab initio* calculations by Parish and Dykstra[13] and by Bulski and Chalasinski.[14] The recent quantum Monte Carlo treatments are due to Mohan and Anderson,[15] who calculated the interaction potential using the diffusion Monte Carlo method (DMC), and due to Tawa, Whitlock, Schmidt, and Moskowitz[16] using variational quantum Monte Carlo methods.

In this paper we present "exact" calculations of the interaction energies of helium trimers in symmetric linear configurations. Unlike DMC calculations the present calculations are free from time-step errors. Second, by writing an efficient vectorized code suitable for C-90, we have been able to reduce the stochastic error bars significantly. A comparison of our present results with those of similar prior calculations of interaction energies for helium dimers[3] enables us to estimate the three-body interaction terms.

We have used the Green's function Monte Carlo method with an efficient cancellation scheme proposed by Anderson, Traynor, and Boghosian.[17] This method has been used successfully in determining the binding energy of a helium dimer[3] and the interaction energy of He–H.[18] It is based on a cancellation scheme first proposed by Arnow *et al.*[19] Here we describe it briefly. First one recasts the Schrödinger equation in its integral form given by

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

where $\mathbf{X}(x_1,x_2,...,x_{3n})$ is the $3N$ dimensional vector, V contains the interelectron and the electron–nucleus potentials. The form of the Green's function $G_0(\mathbf{X},\mathbf{X}')$ is known exactly[20] and is given by

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

where $K_\nu(|\mathbf{X}-\mathbf{X}'|)$ is the Bessel function of imaginary argument.

One starts with a collection of representative wave function samples (psips), usually drawn from a good trial wave function, and samples their moves as indicated in Eq. (2). In order to get a large positive to negative ratio for 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 in close proximity, 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

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

and the Monte Carlo estimate of the energy is given by

$$E = \frac{\Sigma_i s_i w_i \Psi_{T_i}(H\Psi_T/\Psi_T)_i}{\Sigma_i s_i w_i \Psi_{T_i}}, \tag{5}$$

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

The trial wave function is constructed as an antisymmetrized product of Hylleraas $1s^2$ wave functions[21] for helium as follows. With the three helium nuclei denoted as A, B, and C, spin up electrons as 1, 2, and 3, and spin down electrons as 3, 4, and 5, the complete antisymmetric wave function may be written as

$$\Psi = \sum_{n=1}^{36} C_n \cdot P_n \cdot (\phi_{A_{14}} \cdot \phi_{B_{25}} \cdot \phi_{C_{36}} \cdot J_n), \tag{6}$$

where P_n is the permutation operator and C_n is $+1$ and -1 for even and odd numbers of permutations, respectively. The wave function $\phi_{A_{14}}$ is a Hylleraas wave function containing 189 terms due to Schwartz[22] given by

$$\phi_{A_{14}} = \exp(-ks/2) \sum_{l,m,n} C_{lmn} s^l t^n u^m, \tag{7}$$

where $s = r_{1A} + r_{4A}$, $t = r_{1A} - r_{4A}$, $u = r_{14}$, and $k = 3.5$ with $l = 0, \frac{1}{2}, 1, \frac{3}{2}, 2...$etc., $m = 0, 1, 2,...$etc, $n = 0, 2, 4,...$etc. The wave functions $\phi_{B_{25}}$ and $\phi_{C_{36}}$ are similar. The term J_n is the product of the electron–electron and electron–nucleus Jastrow correlation functions and is given by

$$J_{ij} = \exp\left[\frac{(b_1 r_{ij} + b_2 r_{ij}^2)}{(1 + c_1 r_{ij} + c_2 r_{ij}^2)}\right] \tag{8}$$

and

$$J_{iN} = \exp\left[\frac{(b r_{iN})}{(1 + c r_{iN})}\right]. \tag{9}$$

The coefficients b, b_1, b_2, c, c_1, and c_2 were optimized to obtain the minimum variance in local energies.[23]

The details of the calculations were similar to those described for a helium dimer in Refs. 3 and 17. Rotation and reflection operations consistent with the symmetry of the Hamiltonian were carried out in each step. These operations put the psips in a narrower region of the configuration space to allow more effective cancellation. The ratio of positive

TABLE I. Energies for the linear symmetric helium trimer calculated by the "exact" quantum Monte Carlo method.

Separation $r_{AB} = r_{BC}$ (bohrs)	Total energy E_{trimer} (hartrees)
3.5	$-8.704\ 174\ 28 \pm 0.000\ 187\ 6$
4.5	$-8.710\ 755\ 07 \pm 0.000\ 024\ 6$
5.6	$-8.711\ 241\ 34 \pm 0.000\ 006\ 0$
6.5	$-8.711\ 214\ 53 \pm 0.000\ 004\ 2$

psips to negative psips was maintained at about 100 to 1. The preliminary testing and development of the code were carried out 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 250–280 megaflops. The trial wave function and its derivatives for each psip could be calculated independently of the others. Since this part of the calculation, especially for the Hylleraas wave functions, was a major part of the program, efficient vectorization was necessary for efficient utilization of the C-90.

In the discussion of the results, the energies of an isolated helium atom, the dimer, and the trimer are denoted as E_{atom}, E_{dimer}, and E_{trimer}, respectively. Differences in energies, which are the corresponding binding energies, are denoted

$$\Delta E_{dimer} = E_{dimer} - 2E_{atom}, \tag{10}$$

$$\Delta E_{trimer} = E_{trimer} - 3E_{atom}. \tag{11}$$

The term $E_{non-add}$, the nonadditive part of the total energy, is denoted

$$\Delta E_{non-add} = \Delta E_{trimer} - \Delta E_{dimer}^{AB} - \Delta E_{dimer}^{BC} - \Delta E_{dimer}^{CA}, \tag{12}$$

where E_{dimer}^{AB}, E_{dimer}^{BC}, and E_{dimer}^{CA} denote the dimer energies for the helium pairs AB, BC, and CA, respectively.

In Table I we have listed trimer energies for several values of the internuclear distances. In Table II the third column shows the trimer energies if the interaction were pairwise additive. We have calculated this pairwise additive contribution from Ref. 3, wherever possible, and from the compromise potential by Aziz and Slaman.[4] The last column shows $\Delta E_{non-add}$.

In Table III we compare our results with those from prior calculations. The second column refers to the analytic variational calculations due to Parish and Dykstra.[13] This paper

TABLE II. Interaction energy for the symmetric helium trimer by "exact" quantum Monte Carlo method.

$r_{AB} = r_{BC}$ (bohr)	ΔE_{trimer} (K)	$\Sigma \Delta E_{dimer}^a$ (K)	$\Delta E_{non-add}$ (K)
3.5	2201.0 ± 60.0	2225.0 ± 7.0^b	-24.1 ± 70.0
4.5	132.0 ± 7.8	119.0 ± 3.8	12.8 ± 12.2
5.6	-21.5 ± 1.9	-22.3 ± 0.2	0.7 ± 2.1
6.5	-13.1 ± 1.3	-13.8 ± 0.2	0.8 ± 1.3

[a] From Refs. 3 and 4.
[b] Estimated error from Ref. 4.

TABLE III. Comparison of $\Delta E_{\text{non-add}}$ for a linear symmetric trimer

$r_{AB} = r_{BC}$ (bohr)	PD^a (K)	AT^b (K)	NBL^c (K)	Present work (K)
3.5	−2.907	−13.29	12.31	−24.14±60.60
4.5	−0.302	−1.38		−12.81±12.22
5.6	−0.042	−0.19		0.73±2.09
6.5	−0.011	−0.05		0.78±1.34

^{a}From Ref. 13.
^{b}From Ref. 5.
^{c}From Ref. 12.

specifically addresses the issue of importance of pairwise additivity in helium complexes. The values listed in column two are obtained from a fitting formula as given by Parish and Dykstra. The corresponding values for the simple Axilrod–Teller form of Eq. (1) are listed in column three. The coefficient C in the calculation of ΔE^3 in Eq. (1), as has already been mentioned, is directly related to the polarizability of the atoms. For identical atoms, as is the case here, $C = 0.75 \alpha \mu$, where α is the polarizability and μ is the dipole moment. This has been discussed in detail by Midzuno and Kihara.[7] For the helium atoms, $C = 1.6588$ a.u. The only value available for comparison from the SCF calculation of Novaro and Beltran-Lopez[12] is for the nearest-neighbor distance of 3.5 bohrs. Their calculated total energy for the trimer in this case is −8.574 609 a.u., a value significantly higher than the energy of the present calculation. Also, the pairwise nonadditive part is repulsive, as listed in the fourth column. The last column shows our results. For an interatomic distance of 5.6 bohrs, the equilibrium distance for a helium dimer, the corresponding trimer energy is −21.5 ±1.9 K, the nonadditive contribution being 0.7±2.1 K, a few percent of the total binding energy.

To summarize, we have been able to calculate the interaction energy of a helium trimer in symmetric linear configurations by an exact Green's function quantum Monte Carlo method. Compared to the previous diffusion Monte Carlo calculations our error bars are lower by almost an order of magnitude. Calculations of similar accuracies were achieved by Tawa, Whitlock, Schmidt, and Moskowitz[16] for helium trimers in triangular configurations using variational Monte Carlo methods. For all the internuclear distances that we have considered here the estimated nonadditive contribution is found to be a few percent of the total interaction energy.

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