Semiempirical Hyperspherical Model for ^4He_N Clusters

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Received 3 August 2005; accepted 22 August 2005
Published online 31 October 2005 in Wiley InterScience (www.interscience.wiley.com).
DOI 10.1002/qua.20845

ABSTRACT: A semiempirical hyperspherical model for the ground states of low-temperature helium clusters is proposed. Extension of the authors' delta function model for the helium dimer suggests an effective hyper-radial Schrödinger equation with two empirical parameters. The parameters are fitted so as to reproduce the ground-state energies and RMS interatomic distances in Blume and Greene's quantum Monte Carlo computations for ^4He_N clusters with $N = 3$–10. The model can be extrapolated to $N \rightarrow \infty$ to give a reasonable value for the binding energy per atom in a helium droplet.
 Int J Quantum Chem 106: 981–985, 2006

Key words: helium clusters; delta function potential; hyperspherical model; Monte Carlo

Introduction

In recent years, hyperspherical methods have been applied extensively to a wide range of dynamical problems for nuclear, atomic, and molecular systems involving three or more particles. In particular, a large number of recent theoretical studies of low-temperature clusters of helium atoms have been based on adiabatic hyperspherical approximations to the Faddeev equations [1–8]. In addition, Barletta and Kievsky [9] have carried out variational computations using hyperspherical harmonic functions. The present authors [10] have considered a delta function model for the trimer, mainly to explore the analytic properties of the Efimov and Thomas effects. Recently, the Faddeev–Yakubovsky formalism has been applied to the tetramer [11].

The most comprehensive computations to date on helium clusters are those of Blume and Greene [12]. These investigators applied quantum Monte Carlo methods to hyperspherical representations of ground and excited states of ^4He_N clusters for $N = 3$–10. Their results, reexpressed as ε/k_B (in Kelvin), are listed in Table I and shown graphically in Figure 1. Earlier, Pandharipande et al. [13] carried out Monte Carlo computations on helium droplets containing up to several hundred atoms. Their results for the smaller clusters are in essential agreement with those of Blume and Greene.

In the present work, we propose a semiempirical model to reproduce Blume and Greene's ground-state energies, based on a hyperspherical Schröd-

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TABLE I
Parameters for helium clusters.

N	$-\varepsilon_N$/K	r_{rms}/bohr	R_N/bohr	λ_N
3	0.1255	20.52	24.64	4.871
4	0.5568	15.93	26.44	9.260
5	1.296	14.64	28.79	14.14
6	2.309	14.20	31.49	19.53
7	3.565	14.03	34.20	25.34
8	5.019	14.07	37.18	31.67
9	6.677	14.15	39.95	38.33
10	8.495	14.19	40.08	43.44

inger equation with two empirical parameters. We will also show that the $N \to \infty$ limit is consistent with the behavior of macroscopic helium droplets.

Helium Dimer

Our approach is based on a generalization of our model for the helium dimer [14], in which the interatomic potential is approximated by a delta function on a sphere of radius r_0 in the space of relative coordinates, which we have called a "Dirac bubble potential." For zero orbital angular momentum, the relative motion of a pair of helium atoms can be represented by the Schrödinger equation (using atomic units $\hbar = m = e = 1$)

$$\frac{1}{2\mu}\left[-\psi''(r) - \frac{2}{r}\psi'(r) - \frac{\lambda}{r_0}\delta(r - r_0)\psi(r)\right] = \varepsilon\psi(r) \quad (1)$$

with

$$\varepsilon = -k^2/2\mu. \quad (2)$$

The reduced mass $\mu = M/2$, where $M = 7296.293$ atomic units (au) for the ^{4}He atom. For $r \neq r_0$, Eq. (1) has solutions $\psi(r) = \sinh(kr)/r$ and $\psi(r) = e^{-kr}/r$, finite as $r \to 0$ and $r \to \infty$, respectively. The complete wave function must be continuous, but kinked at $r = r_0$, so that the first derivative is discontinuous there. The second derivative will thus contribute a term to match the delta function in the potential energy operator. The (un-normalized) solution to Eq. (1) can accordingly be written

$$\psi(r) = \frac{\sinh(kr_<)e^{-kr_>}}{r} \qquad r_<, r_> \in \{r, r_0\}. \quad (3)$$

The boundary condition at $r = r_0$ is satisfied by matching the $\delta(r - r_0)$ contributions from the kinetic and potential energies. This leads to the relation

$$\frac{2k}{1 - e^{-2kr_0}} - \frac{\lambda}{r_0} = 0 \quad (4)$$

or

$$\lambda = kr_0[1 + \coth(kr_0)], \quad (5)$$

which determines the ground-state energy. Accurate computations by Gentry and coworkers [15], including retardation effects, predicts a $^4He_2$ ground-state energy of $\epsilon = -1.176$ mK. Energies in these low-temperature species are most conveniently expressed in millikelvins, with the conversion factor 1 hartree = 3.1577465×10^8 mK. A delta function potential supports only a single $v = 0$, $J = 0$ bound state, which makes it an appropriate model for the actual $^4He_2$ dimer. Parameters λ and r_0 can be adjusted for optimal fit to Gentry's ground-state energy and wave function, giving $\lambda = 1.07011$, $r_0 = 13.15$ bohr. A bound state for the dimer will exist only for values of $\lambda > 1$.

Hyperspherical Model for Trimer

Generalizing the delta function model to the $^4He_3$ trimer, we will assume that the three particles interact through pairwise potentials of the same form

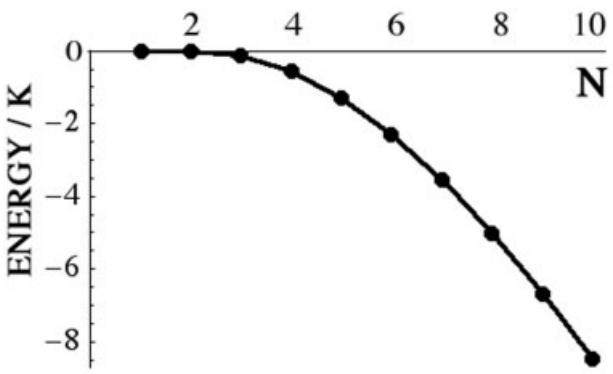

FIGURE 1. Ground-state energies of ^4He_N clusters, from quantum Monte Carlo computations of Blume and Greene [12].

$$V(r_{ij}) = -\frac{\lambda}{Mr_0}\,\delta(r_{ij} - r_0). \tag{6}$$

For compactness of notation, we abbreviate the three interatomic separations using

$$r_1 \equiv r_{23}, \qquad r_2 \equiv r_{31}, \qquad r_3 \equiv r_{12}. \tag{7}$$

The three-particle kinetic energy operator, expressed in terms of the relative interatomic coordinates, is given by

$$T = \frac{1}{M}\left(-\frac{\partial^2}{\partial r_1^2} - \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{r_3^2 - r_1^2 - r_2^2}{4r_1r_2}\frac{\partial^2}{\partial r_1 \partial r_2} + \frac{r_2^2 - r_3^2 - r_1^2}{4r_1r_3}\frac{\partial^2}{\partial r_1 \partial r_3}\right) + \text{cyclic permutations}. \tag{8}$$

For r_1, r_2, $r_3 \neq r_0$, the Schrödinger equation is separable in hyperspherical coordinates R, α_1, β_1. The hyperradius is defined by

$$R \equiv \sqrt{\frac{2}{3}\,(r_1^2 + r_2^2 + r_3^2)}, \tag{9}$$

while

$$\alpha_1 \equiv \alpha \equiv \arcsin(r_1/R), \qquad 0 \leq \alpha \leq \pi/2, \tag{10}$$

and $\beta_1 \equiv \beta$ is the angle between the Jacobi vectors $\mathbf{r}_3 - \mathbf{r}_2$ and $\mathbf{r}_1 - (\mathbf{r}_3 + \mathbf{r}_2)/2$. (Alternative choices of the angular variables are the analogous sets α_2, β_2 or α_3, β_3.) For equilateral triangular configurations of the trimer, we have $\alpha_1 = \alpha_2 = \alpha_3 = \pi/4$. If, in addition, $r_1 = r_2 = r_3 = r_0$, then $R = \sqrt{2}\,r_0 \equiv R_3$.

The ground state of the helium trimer has a rotational angular momentum of zero. There is, of course, no nuclear angular momentum since the helium atoms are spin-zero bosons. It is assumed, in addition, that each atom pair is in an S-state, like diatomic helium. Moreover, the "orbit" of the third atom about each diatomic fragment is assumed to be spherically symmetrical. The wave function is thus independent of the angle between the Jacobi vectors with a separable form in two hyperspherical coordinates:

$$\psi(R, \alpha) = f(R)\phi(\alpha). \tag{11}$$

The Schrödinger separates to two ordinary differential equations:

$$f''(R) + \frac{5}{R}f'(R) - \frac{\mathbf{\Lambda}^2}{R^2}f(R) = k^2 f(R) \tag{12}$$

with

$$\varepsilon = -k^2/M \tag{13}$$

and

$$\phi''(\alpha) + 4\,\cot(2\alpha)\phi'(\alpha) + \mathbf{\Lambda}^2\phi'(\alpha) = 0. \tag{14}$$

The operator $\mathbf{\Lambda}^2$ represents the "grand angular momentum." For bosons, appropriate boundary conditions at $\alpha = 0$ and $\pi/2$, imply GAM eigenvalues given by

$$\mathbf{\Lambda}^2 = \Lambda(\Lambda + 4), \qquad \Lambda = 0, 2, 4\ldots \tag{15}$$

Integration of the wave function over the domain of R and α involves the differential element $R^5\sin^2\alpha\,\cos^2\alpha\,dRd\,\alpha$.

Solutions to Eq. (12) for $\Lambda = 0$ are $R^{-2}I_2(kR)$ and $R^{-2}K_2(kR)$, where I and K are hyperbolic Bessel functions. The potential energy operator

$$V = -\frac{\lambda}{r_0}[\delta(r_1 - r_0) + \delta(r_2 - r_0) + \delta(r_3 - r_0)] \tag{16}$$

spoils the exact separability of the Schrödinger equation. We will consider an effective Hamiltonian in which V is averaged over the hyperspherical angle α to give an equation involving only the hyperradius. This is somewhat analogous to the central-field approximation for atomic orbitals in self-consistent field (SCF) theory. The simplest maneuver is to set $\alpha = \pi/4$, which corresponds to equilateral triangular configurations of the trimer. This gives

$$\frac{\lambda}{r_0}\,\delta(r_1 - r_0) = \frac{\lambda}{r_0}\,\delta\left(\frac{R}{\sqrt{2}} - \frac{R_3}{\sqrt{2}}\right) = \frac{2\lambda}{R_3}\,\delta(R - R_3). \tag{17}$$

Since the three terms in V contribute equally,

$$V_{\text{eff}}(R) \approx -\frac{6\lambda}{R_3}\,\delta(R - R_3). \tag{18}$$

This suggests a representation of the effective hyperradial potential in the form

$$V_{\text{eff}}(R) = -\frac{\lambda_3}{R_3}\,\delta(R - R_3) \tag{19}$$

with λ_3 and R_3 treated as semiempirical parameters.

The effective hyperspherical equation for the trimer is thereby reduced to

$$f''(R) + \frac{5}{R}f'(R) + \frac{\lambda_3}{R_0}\,\delta(R - R_3)\,f(R) = k^2 f(R). \tag{20}$$

An exact solution is given by

$$f_3(R) = R^{-2} I_2(kR_<)\,K_2(kR_>) \qquad R_<,\, R_> \in \{R,\, R_3\}. \tag{21}$$

This function is continuous at $R = R_3$ but has a discontinuous first derivative there. The resultant "kink" implies a second derivative proportional to $\delta(R - R_3)$. This can be matched with the delta function in the potential energy operator when the following condition is satisfied:

$$I_2(kR_3)\,K_2(kR_3) = \lambda_3^{-1}. \tag{22}$$

The assumed trimer ground-state energy $\varepsilon_3 = -125.5$ mK corresponds to a value of $k = 0.05384$. We will describe the assignment of the parameters R_3 and λ_3 in the following section. The condition for a bound state cannot be fulfilled for any other value of $\Lambda > 0$.

Larger Clusters

The quantum state of a ^4He_N cluster depends on $N(N-1)/2$ interatomic displacements r_{ij}, $3N - 6$ combinations of which are independent (e.g., Jacobi coordinates). The definition of the hyperradius for an N-particle system can be generalized to

$$R^2 \equiv 2\sum_{i=1}^{N}(\mathbf{r}_i - \mathbf{r}_{\text{c.m.}})^2 = \frac{2}{N}\sum_{ij}^{N(N-1)/2} r_{ij}^2. \tag{23}$$

The effective hyperradial Schrödinger equations analogous to (20) are

$$f''(R) + \frac{(3N-4)}{R}f'(R) - \frac{\Lambda^2}{R^2}f(R) + \frac{\lambda_N}{R_N}\,\delta(R - R_N)\,f(R) = k_N^2 f(R) \tag{24}$$

with the energies is given by $\varepsilon_N = -k_N^2/M$. All the ground states will be assumed to have $\Lambda^2 = 0$. Thus, in analogy with (21) and (22), the N-dimensional hyperradial equations can be solved to give

$$f_N(R) = R^{-(3N-5)/2} I_{(3N-5)/2}(k_N R_<)\,K_{(3N-5)/2}(k_N R_>) \qquad R_<,\, R_> \in \{R,\, R_N\} \tag{25}$$

subject to the conditions

$$I_{(3N-5)/2}(k_N R_N)\,K_{(3N-5)/2}(k_N R_N) = \lambda_N^{-1}. \tag{26}$$

To determine the parameters λ_N and R_N, we make use of Blume and Greene's computed energies ε_N as well as their results for the root mean square interatomic distance r_{rms}. The latter are also listed in Table I. Note that for $N > 4$, the values of r_{rms} approach the dimer parameter $r_0 = 13.15$ bohr, but they must subsequently increase with cluster size. The expectation value of Eq. (23) gives the relation between the hyperradius and the rms distance:

$$\langle R^2\rangle = \frac{2}{N}\sum_{ij}^{N(N-1)/2}\langle r_{ij}^2\rangle = (N-1)r_{\text{rms}}^2, \tag{27}$$

where

$$\langle R^2\rangle = \frac{\int_0^\infty R^2[f_N(R)]^2 R^{3N-4}dR}{\int_0^\infty [f_N(R)]^2 R^{3N-4}dR}. \tag{28}$$

Using the Monte Carlo results for r_{rms}, we determine values of R_N consistent with Eqs. (27) and (28). Finally, Eq. (26) determines the corresponding λ_N. The resulting parameters R_N and λ_N are listed in Table I.

Extrapolation to $N \to \infty$

The Monte Carlo computations of Pandharipande et al. [13] apply to helium droplets of macroscopic size, represented by the limit $N \to \infty$. The condition (26) determining the N-particle energy can be extrapolated to $N \to \infty$ using uniform asymptotic expansions for Bessel functions. The relevant result is [16]

$$I_\nu(\nu z)\, K_\nu(\nu z) \sim \frac{1}{2\nu\sqrt{1+z^2}} \qquad \text{as} \qquad \nu \to \infty. \quad (29)$$

This applies for $\nu = (3N - 5)/2 \approx (3/2)N$. Let us define

$$\lim_{N\to\infty} \frac{\lambda_N}{N} = \lambda_\infty, \qquad \lim_{N\to\infty} \frac{R_N}{N^{1/2}} = R_\infty, \qquad \lim_{N\to\infty} \frac{k_N}{N^{1/2}} = k_\infty. \quad (30)$$

Thus, we can identify in Eq. (29)

$$z = \frac{2}{3}\, k_\infty R_\infty, \quad (31)$$

and the condition (26) reduces asymptotically to

$$\lambda_\infty = 3\sqrt{1 + \frac{4}{9}\, k_\infty^2 R_\infty^2}. \quad (32)$$

From this relation, along with the data in Table I, the empirical parameters R_N and λ_N can be approximated by:

$$R_N \approx -1.38532 + 13.6125\sqrt{N} \quad (33)$$

$$\lambda_N \approx 20.0081 - 28.2578\sqrt{N} + 11.4514N. \quad (34)$$

The limiting value of ε_N/N as $N \to \infty$ is predicted to be -7.13 K/atom, in almost perfect agreement with the experimental vaporizational energy per atom, -7.12 K/atom. For $N > 4$, the parameters given by (33) and (34) reproduce Blume and Greene's Monte Carlo energies to within 2–3%.

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