Role of three-body interactions in trimer binding[a]

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A semiclassical perturbation expansion is developed for the ground state energy of three identical particles interacting via pair and three-body potentials. The result is applied for the ground state energy of three neon atoms, where the non-pair-additive terms make a small contribution, and for three beryllium atoms where such terms make a large contribution. Models are constructed for the pair and three-body potentials of beryllium, using the results of self-consistent field and dispersion energy calculations. The beryllium dimer and trimer are self-bound.

I. INTRODUCTION

For closed shell atoms it is conventional[1-6] to divide the total potential energy of three atoms into three pair potentials (of isolated pairs) V_2 and a three-body, non-pair-additive potential V_3. At least partly because of the limited information available, V_3 has frequently been approximated by the triple-dipole energy[2,3] of Axilrod, Teller, and Muto. More extensive information on V_3 is now becoming available,[4-6] allowing the construction of more detailed models of V_3 and presenting, in the case of Be$_3$, an example where the three-body term is an appreciable part of the total energy.[6,7]

Here we develop a semiclassical approximation[8] to the ground-state energy of a trimer, including the effects of both V_2 and V_3. We have in mind applications to the ground state of three identical closed shell atoms. As examples we treat the Ne$_3$ trimer, in which V_3 can be regarded as a perturbation on the pair terms, and the Be$_3$ trimer, in which V_3 causes a much more strongly bound trimer than would have been inferred from an analysis with only pair potentials. These are systems in which the configuration of minimum potential energy is an equilateral triangle.

We use models for V_2 and V_3. For neon, there are refined models available[9] for V_2, and because V_3 is a perturbation we construct a simple model of V_3 from Hartree–Fock and dispersion energy results. For beryllium, the available information on V_2 is quite limited. We construct a model V_2 from Hartree–Fock[6,7] and dispersion energy[10] results, using ideas of Slater and Kirkwood[11] and of Buckingham and Corner.[12] The model we construct for V_3 is similar to the Ne$_3$ model.

Murrell and his co-workers[13] have also constructed three-atom potential energy surfaces. For ozone O$_3$, they have determined the parameters by use of spectroscopic data.[14] Here we are treating more weakly bound trimers, for which such data are not available; for beryllium we have had to rely on the results of quantum chemistry calculations,[6,7,10,15,16] and our results are more tentative than theirs.

The organization of the paper is: In Sec. II we pre-

sent the theory and the working equations for the semi-classical ground state energy. In Sec. III we present our results for Ne$_3$. In Sec. IV we present our results for Be$_3$. A summary and conclusions are contained in Sec. V.

II. TRIMER GROUND STATE ENERGY

For three identical particles of mass m we take the Hamiltonian to be

$$H_3 = (p_1^2 + p_2^2 + p_3^2)/2m + V_2(r) + V_2(s) + V_2(t) + V_3(r, s, t). \quad (1)$$

In Eq. (1), r, s, and t are the three interparticle separations and V_2 is the potential energy of an isolated pair of particles; V_3 is the non-pair-additive energy of the three particles and is symmetric in its arguments.

We develop a double perturbation series for the ground state energy of Eq. (1) $E_0(3)$. One expansion parameter is the reduced Planck constant $\hbar$. The ground state we construct is symmetric in the coordinates of the three particles, so it is a three-boson state. For three fermions interacting via pair potentials, it has been shown[17,18] with an analysis similar to ours that the ground state differs from the three-boson ground state by terms in $\hbar^2$.

The second expansion parameter is a parameter λ characterizing the three-body potential V_3. Because we wish to include cases in which V_3 has a large effect on $E_0(3)$ and yet wish to keep the formalism compact, we divide V_3 into two parts

$$V_3 = -K \exp[-\gamma(r + s + t)] + \lambda v_3(r, s, t). \quad (2)$$

The first term on the RHS of Eq. (2) has been found to represent most of the functional dependence in recent self-consistent field (SCF) calculations[5-7] on three closed shell atoms near the equilateral triangle configuration. The second term on the RHS of Eq. (2) represents the deviations from this elementary form, and it is treated as a perturbation in our calculations. For a case such as Ne$_3$, we treat the entire V_3 as a perturbation by setting K equal to zero in our equations.

The expansion in powers of $\hbar$ is a generalization of a previous treatment[8] of the ground state energy of inert gas trimers of the form X_3, in which only pair potentials were included. It is based on an expansion of the total potential energy about the configuration of minimum potential energy and treatment of the deviations from this configuration as harmonic oscillations, corrected for

anharmonic terms in the expansion. In the previous work, carrying the series to $\hbar^2$ terms was found to yield accurate results for Ne_3 and heavier trimers.

For the closed shell atoms studied so far with SCF calculations,[4-7,15,16] the three-particle configuration of minimum total potential energy is apparently an equilateral triangle. For He_3, Ne_3, and Be_3 there is an equilateral triangle which is at least a relative minimum of total potential energy under independent changes of all three interparticle separations. There is no sign in the quantum chemistry calculations for these trimers of nonequilateral configurations of lower energy. Therefore we take as the configuration of minimum total potential energy of three closed shell atoms an equilateral triangle of finite side length L which is determined by the equation

$$\left(\frac{dV_2(r)}{dr} + \frac{\partial V_3(r, s, t)}{\partial r}\Big|_{s,t}\right)_{r=s=t=L} = 0. \tag{3}$$

Ozone is an example where the minimum configuration is iscoceles,[14] not equilateral, and our results do not apply to it.

Next we expand the potential energy in a Taylor series about the equilateral triangle specified by Eq. (3). If the expansion is truncated at terms quadratic in the deviations, the ground state of the Hamiltonian, Eq. (1), can be found exactly as a combination of three harmonic oscillator states. These harmonic oscillators are associated with the usual normal modes[19] of the equilateral triangle; namely, a breathing mode of angular frequency

$$\Omega = \left[(3/m)\left(\frac{d^2V_2}{dr^2} + \frac{\partial^2 V_3}{\partial r^2} + 2\frac{\partial^2 V_3}{\partial r \partial s}\right)_{r=s=t=L}\right]^{1/2}, \tag{4}$$

and a pair of degenerate modes of angular frequency

$$\omega = \left[(3/2m)\left(\frac{d^2V_2}{dr^2} + \frac{\partial^2 V_3}{\partial r^2} - \frac{\partial^2 V_3}{\partial r \partial s}\right)_{r=s=t=L}\right]^{1/2}. \tag{5}$$

On this basis, the beginning of our perturbation series is the ground state energy including the zero-point energy of the normal modes

$$E_{0,h}(3) = 3V_2(L) + V_3(L, L, L) + (1/2)\hbar\Omega + \hbar\omega. \tag{6}$$

To carry the perturbation series to second order in $\hbar$, the cubic and quartic terms in the deviations from the minimum potential configuration must be retained. This is most easily done by writing the deviations in terms of the (harmonic) normal mode coordinates.[19] The calculation is straightforward but lengthy and we only present the final results.

Let the ground state energy $E_0(3)$ be written as

$$E_0 = 3V_2(l) + V_{3,0}(l, l, l)$$
$$+ \hbar E(1, 0) + \hbar^2 E(2, 0) + \lambda E(0, 1)$$
$$+ \lambda^2 E(0, 2) + \lambda\hbar E(1, 1) + \cdots \tag{7}$$

The notation $E(i, j)$ means ith order in $\hbar$ and jth order in λ. The separation l and the subscript zero on $V_{3,0}$ mean these are to be obtained from Eqs. (2) and (3) with λ set equal to zero. Similarly the frequencies Ω_K and ω_K are obtained from Eqs. (4) and (5) as

$$\Omega_K = \left[\left(\frac{3}{m}\right)\left(\frac{d^2V_2}{dr^2} + 3\frac{\partial^2 V_{3,0}}{\partial r^2}\right)_{r=s=t=l}\right]^{1/2}$$

$$\omega_K = \left[\left(\frac{3}{2m}\right)\frac{d^2V_2}{dr^2}\Big|_{r=l}\right]^{1/2}. \tag{8}$$

The coefficients shown in Eq. (7) are

$$E(1, 0) = (\Omega_K/2) + \omega_K; \tag{9}$$

$$E(2, 0) = -(6m)^{-3}(4\alpha^2\{(\omega_K\Omega_K)^{-2} + [\Omega_K\,\omega_K^2(\Omega_K + 2\omega_K)]^{-1}\}$$
$$+ 8\beta^2\omega_K^{-4} + 11\gamma^2\Omega_K^{-4} + 12\alpha\gamma(\Omega_K^3\omega_K)^{-1})$$
$$+ (6m)^{-2}[(A/\Omega_K^2) + (B/\Omega_K\omega_K) + (C/\omega_K^2)]; \tag{10}$$

$$E(0, 1) = v_3(l, l, l); \tag{11}$$

$$E(0, 2) = -(9/2m\Omega_K^2)[\partial v_3/\partial r]^2; \tag{12}$$

and

$$E(1, 1) = (3/4m)(\partial^2 v_3/\partial r^2)[(1/\Omega_K) + (1/\omega_K)]$$
$$+ (3/2m)(\partial^2 v_3/\partial r \partial s)[(1/\Omega_K) - (1/2\omega_K)]$$
$$+ (3/4mr\omega_K)(\partial v_3/\partial r)$$
$$- (1/m^2\,2\sqrt{3})(\partial v_3/\partial r)[2\alpha(\omega_K\,\Omega_K^2)^{-1} + 3\gamma\Omega_K^{-3}], \tag{13}$$

where the coefficients in Eqs. (10) and (13) are defined by

$$\alpha = [9\sqrt{3}/4][d^3V_2/dr^3 + (1/r)d^2V_2/dr^2$$
$$+ (3/r)\partial^2 V_{3,0}/\partial r^2] \tag{14a}$$

$$\beta = [3\sqrt{3}/8][-d^3V_2/dr^3 + (3/r)d^2V_2/dr^2] \tag{14b}$$

$$\gamma = [3\sqrt{3}/2](d^3V_2/dr^3 + 9\,\partial^3 V_{3,0}/\partial r^3) \tag{14c}$$

$$A = (27/8)(d^4V_2/dr^4 + 27\,\partial^4 V_{3,0}/\partial r^4) \tag{14d}$$

$$B = (27/4)[d^4V_2/dr^4 + (1/r)d^3V_2/dr^3 - (2/r^2)d^2V_2/dr^2$$
$$+ (9/4r)\,\partial^3 V_{3,0}/\partial r^3 - (6/r^2)\partial^2 V_{3,0}/\partial r^2] \tag{14e}$$

$$C = (27/8)[d^4V_2/dr^4 + (2/r)d^3V_2/dr^3$$
$$- (1/r^2)d^2V_2/dr^2 + (6/r^2)\,\partial^2 V_{3,0}/\partial r^2], \tag{14f}$$

and all the functions in Eqs. (12)–(14) are to be evaluated at $r = s = t = l$.

Equations (7)–(14) constitute the semiclassical expansion we use for the trimer ground state energy. In the absence of V_3 they reduce to the result used earlier[8] for inert gas trimers: For particles interacting via Lennard–Jones 12–6 potentials

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \tag{15}$$

and with a deBoer parameter Λ^* defined by

$$\Lambda^* = 2\pi\hbar/(m\epsilon\sigma^2)^{1/2}, \tag{16}$$

the trimer ground state energy is

$$E_0(3) = 3\epsilon[-1 + 0.83849\,\Lambda^* - 0.20419\,\Lambda^{*2} + \Theta(\Lambda^{*3})]. \tag{17}$$

III. THREE-BODY INTERACTION AS A PERTURBATION

The pair potential V_2 of neon[9] has a minimum of depth 42.0 K (1.33×10^{-4} a.u.) at a separation of 3.10 Å (5.86 a.u.). The scale of energy of the Axilrod–Teller–Muto

triple-dipole potential,[2,3,20] and of extrapolations of the Novaro–Nieves[5] SCF calculation of V_3, is much smaller than this at such separations, so that is a good approximation to consider the entire V_3 as a perturbation in the determination of $E_0(3)$. We now make this more precise.

For V_2 we take the Morse potential

$$V_2(R) = \epsilon\{\exp[-2\beta(x-1)] - 2\exp[-\beta(x-1)]\}$$

$$x = R/R \text{ min} \tag{18}$$

$$\epsilon = 58.0\times10^{-16}\,\text{erg};\ R_{\min} = 3.102\ \text{Å};\ \beta = 6.27.$$

This is the potential bowl of the ESMSV–III potential[9] (and also of the MSV–II potential), constructed to fit a variety of neon thermodynamic and molecular scattering data.[9]

For V_3 we use the triple dipole potential[2,3] of Axilrod, Teller, and Muto and an estimate of the exchange–overlap contribution based on SCF calculations of Novaro and co-workers.[5,7] The triple-dipole potential for a triangular configuration of sides r, s, and t and internal angles θ_1, θ_2, and θ_3 is

$$V_{3td} = 3Z(1, 1, 1)(rst)^{-3}(1 + 3\cos\theta_1\cos\theta_2\cos\theta_3). \tag{19}$$

For Ne$_3$, we use the value

$$Z(1, 1, 1) = 4.25\ \text{a.u.}, \tag{20}$$

taken from the estimates of Tang et al.[20]

Novaro and Flores[7] have supplemented earlier[5] Ne$_3$ SCF calculations with values for V_3 in three more equilateral triangle configurations. For side 3 a_0 they find -1.33×10^{-2} a.u.; for 3.5 a_0, -2.24×10^{-3} a.u.; for 4 a_0, -1.83×10^{-4} a.u. Combining these values with the Novaro–Nieves values and extrapolating on a semilogarithmic plot (i.e., with an exponential fit to the distance dependence), we obtain an estimate for V_3 in the equilateral triangle of side 5.9 a_0: -2 to -7×10^{-8} a.u. This is small compared to the value 2×10^{-6} a.u. of V_{3td} in the same configuration. Therefore, we neglect the SCF contribution to V_3 and take V_{3td}, Eqs. (19) and (20) as our approximate model for V_3 of Ne$_3$.

In the equilateral triangle of side l, we have for the partial derivatives which enter in Eqs. (12) and (13)

$$\partial v_3/\partial r = \partial V_{3td}/\partial r = -12.375\,Z(1, 1, 1)/l^{10};$$

$$\partial^2 v_3/\partial r^2 = \partial^2 V_{3td}/\partial r^2 = 40.5\,Z(1, 1, 1)/l^{11}; \tag{21}$$

$$\partial^2 v_3/\partial r\,\partial s = \partial^2 V_{3td}/\partial r\,\partial s = 41.625\,Z(1, 1, 1)/l^{11}.$$

The series for the trimer ground state energy is obtained from Eqs. (7)–(14), dropping $V_{3,0}$, taking L equal to 3.102 Å, and using 3.35×10^{-23} gm for the mass of the Ne atom. The terms in the series are

$$E(0, 0) = 3V_2(R_{\min}) = -126.0\ \text{K},$$

$$\hbar E(1, 0) = +60.1\ \text{K},$$

$$\hbar^2 E(2, 0) = -7.1\ \text{K},$$

$$\lambda E(0, 1) = 0.7\ \text{K},$$

$$\lambda^2 E(0, 2) = -2\times10^{-3}\ \text{K},$$

$$\lambda\hbar E(1, 1) = -0.27\ \text{K},$$

with a sum

$$E_0(3) \simeq -72.6\ \text{K}.$$

As expected the terms in λ and λ^2 are much smaller than the others. The fractional contribution of the $\hbar$ and $\hbar^2$ terms to $E_0(3)$ is similar to the contribution found[8] for the Ne$_3$ trimer using Lennard–Jones 12–6 pair potentials.

IV. SIGNIFICANT THREE-BODY INTERACTION:

Recent calculations[6,7,15,16] of the ground state electronic energy surface of small clusters of beryllium atoms show there are strong deviations from pairwise additivity of the atomic energies. Self-consistent field calculations for clusters of the nominally closed shell Be atoms show the ground state energies of Be$_2$ and of Be$_3$ are lowest for atoms at infinite separations,[6,16] while for Be$_4$ a minimum is found[15] in a tetrahedral configuration of interatomic spacing 2.1 Å (4.0 a_0). A study of the energy surface of Be$_3$ near the 4 a_0 spacing[6] shows the V_3 energy is an appreciable fraction of the total V_2 energy.

Here we estimate the effects of V_3 in the ground state energy $E_0(3)$ of the Be$_3$ trimer. For this, we construct models for V_2 and V_3 by combining information from the SCF calculations with dispersion energy terms. Our construction is more uncertain than constructions[21] of V_2 for inert gas dimers from such information because the multipole series[10] for V_2 (Be$_2$) appears to be more slowly convergent than for the inert gases[20] and because, as we discuss below, the large values of V_3 (Be$_3$) make final results sensitive to the modeling of the repulsive wall of V_2. We do obtain a model V_2 with a weak attractive well capable of binding the Be$_2$ dimer.

More basic than the uncertainty in modeling V_2 and V_3 is the question of the validity of using a Hamiltonian such as Eq. (1) to describe the atomic motions in Be clusters. The use of Eq. (1) is based on assuming the validity of the Born–Oppenheimer approximation[1]; that is, assuming that in motions of the atomic nuclei the electrons follow in their ground state. This would not appear to be the case for a metal, where some of the electrons become delocalized from the atom; however SCF calculations on the electronic ground state of Be clusters show that electrons are not appreciable delocalized for clusters of fewer than twenty atoms.[22] A second criterion is whether there are crossing or near crossings of atomic excited-state energy surfaces with the ground state energy surface. There are no calculations showing this phenomenon for Be$_3$. For other alkaline earth dimers Mg$_2$ and Ca$_2$, there are spectroscopic observations[23,24] showing that the interaction energy of the excited state and ground state atom narrows the separation of the energy surfaces but still leaves a sizable gap between them.

We proceed with the treatment of Be$_3$ within the Born–Oppenheimer approximation, with the qualification that corrections to the Born–Oppenheimer approximation may be appreciable and that they certainly should be estimated when more information is available.

Our construction of the Be_2 pair potential follows constructions used by Slater and Kirkwood[11] and by Buckingham and Corner[12] for helium. The first step is to approximate V_2 by a linear combination of a repulsive taken from SCF calculations and an attraction taken from dispersion energy calculations

$$\tilde{V}_2(R) = Ae^{-\alpha R} - (C_6/R^6), \qquad (22)$$

with

$A = 3.03$ a.u.

$\alpha = 1.07$ a.u.

$C_6 = 214$ a.u.

We use the Maeder–Kutzelnigg[10] value for C_6 and have fitted the exponential to the Kølos et al. Be_2 SCF calculations[6] at 6 and 8 a_0.

There is a potential minimum for $\tilde{V}_2$ of -2.36×10^{-4} a.u. at $R_e = 8.1\ a_0$. At smaller separations $\tilde{V}_2$ shows a failing common to such models[1]; the dispersion energy dominates over the overlap repulsion. Therefore we have introduced a damping factor for the dispersion energy inside the potential minimum

$$V_2(R) = \begin{cases} \tilde{V}_2(R), & R \geq R_e, \\ Ae^{-\alpha R} - (C_6/R^6)\exp\{-B[(R_e/R)-1]^5\}, & R < R_e \end{cases} \qquad (23)$$

with A, α, and C_6 as in Eq. (22) and $B = 290$. We determined the value by B by setting the damped dispersion energy to be 20% of the SCF energy at 6 a_0; the power law in the damping was chosen to give a potential V_2 with continuous fourth derivative.

We found recently proposed constructions[21] of V_2 from similar data for inert gases not to be helpful for Be_2. The higher multipole coefficients of Maeder and Kutzelnigg[10] show the multipole series to be slowly convergent near 8 a_0, so we retained only the first term of this asymptotic series. Because V_3 is an appreciable fraction of $3V_2$ in the SCF calculations on Be equilateral triangles,[6] we need to damp the dispersion energy term in V_2 strongly in the region of the medium energy pair repulsion. That is a requirement not encountered in the inert gas constructions[12,21] and the damping factors used there are not strong enough for our purpose.

We estimate the dimer binding energy for Be, $E_0(2)$, to be 1.2×10^{-7} a.u. (38 K), using an $\hbar^2$ series similar to the series of Sec. II. The fractional contribution of zero point energy is similar to the case of the neon dimer.

For V_3 we use a linear combination of the triple-dipole potential Eq. (19) and a fit to the SCF calculations of Novaro et al.[6,7]

We estimate the coefficient $Z(1, 1, 1)$ in Eq. (19) for Be_3 using the Drude model approximation[25] in terms of the atomic polarizability α and the dipole–dipole strength C_6

$$Z(1, 1, 1) \simeq \alpha C_6/4. \qquad (24)$$

Using α calculated by Stevens and Billingsley[26] and C_6 calculated by Maeder and Kutzelnigg[10] we have

$$Z_{Be}(1, 1, 1) \simeq 2.0 \times 10^3 \text{ a.u.} \qquad (25)$$

The SCF results of Novaro and Flores[7] for configurations of Be_3 near the equilateral triangle of side 4 a_0 can be fitted well by the exponential function used in Eq. (2). Results for non-equilateral configurations about the equilateral triangles of side 6 to 8 a_0, which would be needed for a detailed study of the Be_3 ground state, are not available. We therefore use the exponential function of Eq. (2) as our model for the SCF contribution to V_3 and fit the parameters to the Kølos et al.[6] results for the 6 and 8 a_0 equilateral triangles.

The resulting model for V_3 is (in a.u.)

$$V_3(Be) = -44.2 \exp[-0.504(r+s+t)]$$
$$+ 6 \times 10^3\,(rst)^{-3}(1 + 3\cos\theta_1\cos\theta_2\cos\theta_3), \qquad (26)$$

with the same notation as in Eq. (20). For near-equilateral configurations of particle spacings 6–8 a_0, the SCF component is the dominant part of V_3, with the second term on the RHS of Eq. (26) being less than 25% of the first term. The SCF component is a significant fraction of the pair energy of Eq. (23). Therefore, as in Sec. II, we include the SCF component in the analysis determining the normal modes and we include the effect of the triple-dipole potential by a perturbation expansion.

Using Eqs. (23) and (26), the equilateral triangle for which $3V_2(R) + V_{3,0}$ is minimum has side length 6.98 a_0. This is the separation denoted by l in Sec. II. (Including the triple-dipole repulsion in the minimization increases the separation by 0.1 a_0; comparing that shift to the 1 a_0 shift from the pair potential minimum is another demonstration that the SCF component is the dominant part of V_3.)

The terms in the series Eq. (7) are

$$E(0, 0) = 3V_2(l) + V_{3,0}(l, l, l) = -1.35 \times 10^{-3} \text{ a.u.},$$

$$\lambda E(0, 1) = +2.10 \times 10^{-4} \text{ a.u.},$$

$$\hbar E(1, 0) = +6.84 \times 10^{-4} \text{ a.u.},$$

$$\lambda^2 E(0, 2) = -9.6 \times 10^{-6} \text{ a.u.},$$

$$\hbar^2 E(2, 0) = -1.2 \times 10^{-4} \text{ a.u.},$$

$$\lambda\hbar E(1, 1) = +1 \times 10^{-7} \text{ a.u.},$$

and the net ground state energy is

$$E_0(3) \simeq -5.86 \times 10^{-4} \text{ a.u.} \quad (185 \text{ K}).$$

In the evaluation of $E(1, 1)$ there has been a large mutual cancellation of the contributions of the terms in Eq. (13). Apart from the perhaps fortuitous reduction in the magnitude of $E(1, 1)$, these values should be a good reflection of the relative contributions of the terms in Eq. (7). The series in Eq. (7) appears to converge quite satisfactorily.

The large effect of the pair non-pair-additive interaction V_3 in the binding of Be_3 is shown in the shift of the minimum potential separation to 7 a_0 from the pair minimum of 8.1 a_0 and in the trimer ground state energy of -5.9×10^{-4} a.u. compared to the dimer energy of -1.2×10^{-4} a.u.

As remarked in Sec. II, the ground state we have constructed is a three-boson state. Our calculations are actually for the stable isotope ^{9}Be, a fermion. We use a semiclassical estimate[17,18] for the shift in the ground state energy of three spin-1/2 fermions to estimate this effect here: $3\hbar/2mL^2$. The shift obtained is 1.9×10^{-6} a.u., or less than 1/2% of our value of $E_0(3)$, and we neglect it compared to the uncertainty of at least 25% in $E_0(3)$ resulting from the ambiguities in the construction of our models for V_2 and V_3.

V. SUMMARY AND CONCLUSIONS

We have developed a semiclassical perturbation expansion for the ground state energy of three identical closed shell atoms, allowing for appreciable contributions from explicit three-body non-pair-additive interactions. In application to neon and beryllium trimers the expansion appears to converge quite satisfactorily.

We have constructed models for the pair and three-body potentials, V_2 and V_3, of beryllium from self-consistent field and dispersion energy results. A novel feature in the construction is the sensitivity because of the large relative magnitude of V_3, of the ground state energy to the modeling of the medium energy repulsion in V_2. We find the beryllium dimer and trimer are self-bound and that the ground state energy of the trimer is 50% larger in magnitude than we would have inferred from the use of only our model for V_2.

In small beryllium clusters there are, as has been noted by others,[6,15,16] large and significant deviations from the pairwise additivity of interatomic interactions. There is also a prospect that there are significant corrections to be made to a treatment, such as ours, of the atomic motions using the Born–Oppenheimer approximation. These questions may be resolved as more quantitative information becomes available on the interaction of small numbers of beryllium atoms.

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