# Three-Body Contribution to Binding Energy of Solid Argon and Analysis of Crystal Structure

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The binding energy of solid argon has been computed using a symmetry-adapted perturbation theory three-body potential. This energy equals $-7752.9$ J/mol and agrees well with the experimental value of $-7726 \pm 13$ J/mol. The fcc structure is favored over the hcp structure by 0.01%, in agreement with experimental observations. In accord with an early suggestion of Jansen [Adv. Quantum Chem. **2**, 119 (1965)], inclusion of nonadditive exchange contributions were found to be necessary to understand the preferred crystal structure and for accurate computation of the binding energy. [S0031-9007(97)03748-4]

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The binding energy, crystal structure, and lattice constant of rare gas solids have for a long time been accurately known from experiments and in particular the first two quantities were heavily studied theoretically. The first attempts at analyzing the solid form of the rare gases approximated the many-body potential by the two-body, i.e., pairwise additive contribution. In this approximation the binding energies of the heavier rare gases were predicted to be between 4% (Ne) and 9% (Xe) too low compared to experimental values [1]. Such theory also predicted the hcp crystal structure to be about 0.01% more stable than the observed fcc structure [2]. Since current two-body potentials for rare gas atoms are believed to be very accurate, their residual errors cannot be responsible for these discrepancies. The first attempts to incorporate many-body effects into the binding energy calculations came from Axilrod and Teller [3] and Muto [4] who approximated the three-body nonadditivity by the first term in the multipole expansion of the third-order dispersion energy, called the ATM or triple-dipole (*ddd*) term. This approach worked remarkably well in explaining the discrepancies in binding energies which were reduced by inclusion of the ATM term to about $\pm 1\%$, compared to the experimental accuracy of 0.4%–0.1%; however, the predicted crystal structure remained to be of the hcp type. Further attempts were made to improve the many-body potential by considering higher-order terms in the multipole expansion of the third-order dispersion energy [5], i.e., terms which involve *ddq*, *ddo*, *dqq*, and *qqq* interactions, where *q* and *o* denote quadrupole and octupole moments, respectively. The contributions from these higher-order terms were found to be significant but did not necessarily improve agreement between theory and experiment. The computations mentioned above neglected the charge overlap damping effects present in the third-order dispersion energy. This problem was investigated for $H_3$ by O'Shea and Meath [6] who found the ATM term to be damped by about 15%–40% at equilibrium separations. However, the damped dispersion energies have never been applied in crystal structure calculations. Jansen investigated the three-body nonadditivity of the first- and second-order exchange energies [7] and found the exchange energy components to be very large, making the fcc structure more stable than hcp by as much as 4%. However, the approximate method of Jansen significantly overestimated the exchange nonadditivities, as shown by Refs. [8,9]. The first-order exchange nonadditivities for selected geometries of rare gas trimers were reliably computed almost twenty years ago [10,11]. Although Meath and Aziz pointed out in their 1984 paper [12] that for equilateral triangle geometries the first-order exchange effects nearly cancel the contribution from the dispersion nonadditivity, which should lead to a significant worsening of agreement with experiment, these components were never used in a complete calculation of crystal binding energy. In particular the latest such calculation for argon, published in 1986 by Aziz and Slaman [13], did not include any three-body exchange effects. Incorporation of higher than third-order dispersion nonadditivities [14,15], which take into account also four-body and higher nonadditive contributions, gave relatively small improvements (this work was based on an oscillator model recently shown to be incorrect [16]). It was also attempted to resolve the crystal structure problem by consideration of the zero-point energy [17]. The results of such computations predicted a difference of 0.01% in the zero-point energies favoring the fcc lattice. Since the zero-point energy contributes only about 10% to the binding energy, this difference is negligible. Thus, observation that the heavy rare gas solids crystallize in the fcc rather than the hcp structure has never been explained satisfactorily, and is sometimes referred to as the "crystal structure paradox" [2,18].

We have computed an *ab initio* three-body potential for the Ar trimer based on the nonadditive symmetry-adapted perturbation theory (SAPT) developed in Ref. [19]. Large orbital basis sets were used. Details of these calculations are published elsewhere [16]. The SAPT method included the third-order dispersion nonadditivity $E^{(3)}_{\mathrm{disp}}[3,3]$ with a complete account of charge overlap effects. In addition the fourth-order dispersion nonadditivity $E^{(4;0)}_{\mathrm{disp}}[3,3]$, which had been estimated before only in a crude approximation [14], has been computed *ab initio*. The first-order exchange nonadditivity has been obtained directly, as well as included via the Hartree-Fock nonadditivity $E_{\mathrm{int}}^{\mathrm{HF}}[3,3]$. The latter quantity takes into account also the induction and exchange-induction effects up to infinite order. The second-order exchange-dispersion nonadditivity, $E_{\mathrm{exch-disp}}^{(2;0)}[3,3]$, has been calculated as well. It is believed that these contributions account for all significant physical effects in $\mathrm{Ar}_3$ interaction. The SAPT computed energies were fitted to an analytic potential. This potential is expected to be significantly more accurate than anything available so far.

The binding energy of a crystal consists of a static component which can easily be computed by summing the two- and three-body contributions over the lattice and of the zero-point vibrational energy. The latter quantity was calculated in the quartic oscillator approximation as used in Refs. [13,20–23]. Expanding the potential that an atom in a crystal experiences due to its fixed (Einstein approximation) neighbors through quartic terms, allows the Schrödinger equation for the motion of this atom to be written as [20,22]

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + P_0 + P_2(x^2 + y^2 + z^2) + P_4(x^4 + y^4 + z^4)\right]\Psi = E\Psi\,, \qquad (1)$$

where $m$ is the mass of argon atom. In the present work only two- and three-body contributions to the binding energy will be considered so that $P_0$, $P_2$, and $P_4$ are sums of two- and three-body components, $P_i = P_i[2,N] + P_i[3,N]$, $i = 0,2,4$, where $X[K,N]$ denotes the $K$-body contribution to the $N$-body quantity. The first term, $P_0$, represents the static potential energy at the equilibrium position of the $i$th atom and is the sum of the two- and three-body contributions

$$P_0 = \sum_{\substack{j \\ j\neq i}} v_2(r_{ij}) + \sum_{\substack{j>k \\ j,k\neq i}} v_3(r_{ij}, r_{jk}, r_{ik})\,, \qquad (2)$$

where two- and three-body potentials depend on interatomic distances. The total static binding energy per atom $E_S$ is one-half of the two-body term plus one-third of the three-body term. The harmonic constant $P_2$ is obtained from the Taylor expansion of $P_0$ [20–22]:

$$P_2[2,N] = \tfrac{1}{6}\sum_{j\neq i}[v_2''(r_{ij}) + 2v_2'(r_{ij})/r_{ij}]\,, \qquad (3)$$

$$P_2[3,N] = \tfrac{2}{3}\sum_{\substack{j>k \\ j,k\neq i}}\Big[\partial^2 v_3/\partial r_{ij}\partial r_{ik}(\hat{\mathbf{r}}_{ij}\cdot\hat{\mathbf{r}}_{ik}) + \tfrac{1}{2}\,\partial^2 v_3/\partial^2 r_{ij} + \tfrac{1}{2}\,\partial^2 v_3/\partial^2 r_{ik} + \frac{1}{r_{ij}}\,\partial v_3/\partial r_{ij} + \frac{1}{r_{ik}}\,\partial v_3/\partial r_{ik}\Big]. \qquad (4)$$

Since the anharmonic contribution dependent on the quartic constant $P_4$ is small, this constant was computed using only the pairwise additive part of the potential. Following Refs. [20,22] we get

$$P_4 = \frac{1}{72}\sum_{\substack{j \\ j\neq i}}\left(v_2^{iv}(r_{ij}) + 4\,\frac{v_2^{iii}(r_{ij})}{r_{ij}}\right). \qquad (5)$$

Notice that this expression involves a further approximation consisting of replacing $x^2y^2 + x^2z^2 + y^2z^2$ terms in the Taylor expansion by $x^4 + y^4 + z^4$ [20]. If thermal effects are ignored and the eigenvalues of Eq. (1) are solved for using first-order perturbation theory, the Helmholtz free energy per atom can be expressed as [20,23]

$$\begin{aligned}\tilde{F} &= E_S + \tfrac{3}{2}[\hbar(2P_2/m)^{1/2} + 3\hbar^2 P_4/(4mP_2)] \\ &= E_S + E_Z^H + E_Z^{AH}.\end{aligned} \qquad (6)$$

The second and third terms represent the harmonic and anharmonic contributions to the zero-point energy, respectively. Since the two-body contribution is much larger than the three-body one, in order to separate them the square root in Eq. (6) can be expanded

$$\begin{aligned}E_Z^H &\approx \tfrac{3}{2}\sqrt{2P_2[2,N]/m}\left(1 + \frac{P_2[3,N]}{2P_2[2,N]}\right) \\ &= E_Z^H[2,N] + E_Z^H[3,N].\end{aligned} \qquad (7)$$

The Einstein approximation of fixed neighbors can be removed using the approach of Domb and Salter [24]. This results in multiplying the Einstein approximation value by a constant $C = \sqrt{15/16} = 0.9682$. A more accurate value of this constant can be inferred from numerical calculations of Isenberg [25] and it is equal to 0.964 21. We will follow most recent calculations [13,23] and multiply the complete zero-point energy by $C$.

All contributions have been computed for argon atoms in fcc and hcp configurations with $N \approx 8000$ corresponding to a cubic crystal with 20 atoms per side. The nearest neighbor separation was varied from 6.0 to 7.5 bohr. The additive contributions have been computed using the HFDID1 potential of Aziz [26]. The additive and nonadditive contributions to the binding energy of fcc solid argon are shown in Fig. 1 and Table I for the nearest neighbor distance of 7.088 bohrs, which is the minimum of our binding energy. The three-body nonadditive contribution for the fcc lattice is 561.8 J/mol while the additive one is $-8314.7$ J/mol, showing that the nonadditive effects decrease the magnitude of the binding energy by about 7%. This means a significant amplification compared to the Ar trimer where the nonadditive effects are responsible for only about 1% of the binding at the minimum. The total binding energy was found to be $-7752.9$ J/mol which is 0.3% larger in magnitude than the experimental value of $-7726 \pm 13$ J/mol [1]. Figure 1 shows that the nearest neighbor separation is quite significantly affected by the nonadditivity. Consideration of additive contribution alone predicts the nearest neighbor separation of 7.034 bohrs, which is about 1% smaller

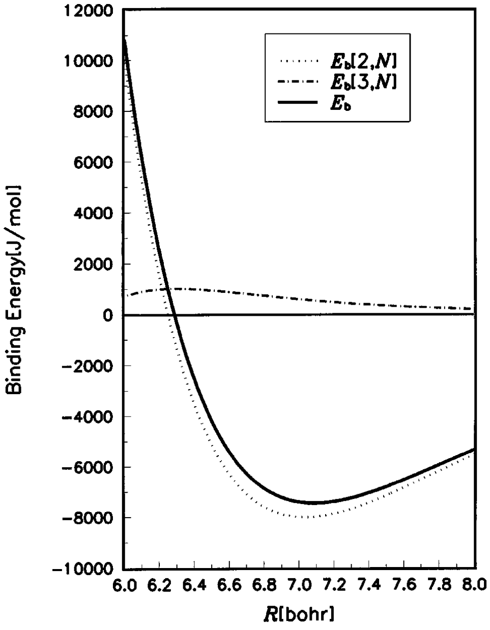

FIG. 1. Dependence of additive and three-body nonadditive contributions to the binding energy of fcc argon on nearest neighbor separation.

than the experimental value of 7.097 bohrs [28]. Including the three-body nonadditive contribution increases the nearest neighbor separation to 7.088 bohrs, which is only 0.1% different from the experimental value. The experimental value is likely to be slightly too large due to the presence of imperfections in the solid argon samples used in measurements so that the computed value may in fact be closer to the "true" nearest neighbor separation in the ideal crystal than this comparison would indicate.

The additive potential from Ref. [26] is not realistically separated into physical components so that decomposition of the additive contributions to the binding energy is not possible. However, the three-body nonadditive SAPT potential consists of components with clear physical interpretation which are shown in Fig. 2 and listed in Table I. It is clear that the three-body contribution cannot be quantitatively described by one component alone. The largest component, the third-order dispersion energy, overestimates the nonadditive binding energy by about 30%. The exponentially decaying components are large. The contributions from the Hartree-Fock nonadditivity (which consists mostly of the first-order exchange energy) and the fourth-order dispersion nonadditivity are canceled to a large degree by the second-order exchange-dispersion contribution explaining the relative success that additive +ATM models enjoyed. The three-body contribution to the harmonic zero-point energy is almost negligible due to significant cancellations between physical components.

Table I shows substantial differences between the latest computation of binding energy of argon [13] and that of the present work. The additive contributions to the static and zero-point components of the binding energy are 10.5 and 8.5 J/mol apart, respectively. This reflects solely the variance in the two-body potentials of Refs. [13,26] (in fact, for the same $R$ of 7.09687 bohrs the difference in $E_S[2,N]$ is still larger amounting to 25.2 J/mol). Much more substantial differences exist between the three-body contributions to the static and zero-point energies. The former energies differ by 82.6 J/mol which is over 1% of the binding energy, while the latter by 19.8 J/mol. The third-order dispersion contributions are very close, which is due to the remarkable closeness between the multipole expanded and unexpanded third-order dispersion nonadditivities [16]. Substantial disagreement exists between contributions from fourth-order dispersion nonadditivity. However, we have shown [16] that the method of approximating fourth-order dispersion nonadditivity used in Refs. [14,23] is incorrect. The Hartree-Fock nonadditivity and the second-order exchange-dispersion nonadditivity, which were not included in previous work, give very large contributions amounting in magnitude to about 3% and 5%, respectively, of the total binding energy.

TABLE I. Binding energy contributions for argon at 0 K. The present values were computed using a nearest neighbor separation of 7.088 bohrs while those of Aziz and Slaman [13] used a nearest neighbor separation of 7.09687 bohrs. All energies are in J/mol.

| Component | Aziz-Slaman | Present-fcc | Present-hcp |
|---|---|---|---|
| $E_S[2,N]$ | −9093.4 | −9082.9 | −9083.2 |
| $E_S[3,N]$ | 652.2 | 569.6 | 570.5 |
| $E_{\mathrm{int}}^{HF}[3,N]$[a] | ··· | −226.2 | −225.6 |
| $E_{\mathrm{exch-disp}}^{(2;0)}[3,N]$[a] | ··· | 378.3 | 378.6 |
| $E_{\mathrm{disp}}^{(3)}[3,N]$[a] | 801.2[b] | 805.0 | 805.3 |
| $E_{\mathrm{disp}}^{(4;0)}[3,N]$[a] | −149.0[c] | −387.5 | −387.8 |
| $E_Z^H[2,N]$ | 744.3 | 752.8 | 752.8 |
| $E_Z^H[3,N]$ | 12.0 | −7.8 | −7.7 |
| $E_{\mathrm{int}}^{HF}[3,N]$[d] | ··· | −29.4 | −29.4 |
| $E_{\mathrm{exch-disp}}^{(2;0)}[3,N]$[d] | ··· | 21.3 | 21.3 |
| $E_{\mathrm{disp}}^{(3)}[3,N]$[d] | 12.0[e] | 12.3 | 12.4 |
| $E_{\mathrm{disp}}^{(4;0)}[3,N]$[d] | ··· | −12.0 | −12.0 |
| $E_Z^{AH}[2,N]$ | 21.9[f] | 15.4 | 15.5 |
| $E_b$[g] | −7663.0 | −7752.9 | −7752.1 |

[a] Physical contributions to $E_S[3,N]$.
[b] Sum of *ddd*, *ddq*, *qqd*, *ddo*, and *qqq* undamped asymptotic contributions. The *ddd* (ATM) contribution was 571.6 J/mol.
[c] Approximate Drude model contribution from Bell and Zucker which includes also higher than three-body effects [23].
[d] Physical contributions to $E_Z^H[3,N]$.
[e] Computed using components in footnote a. The ATM contribution was 7.4 J/mol.
[f] Computed using the ratio of anharmonic to harmonic contributions from the Morse potential of Glyde [27].
[g] Experimental value from Ref. [1] is −7726 ± 13 J/mol.

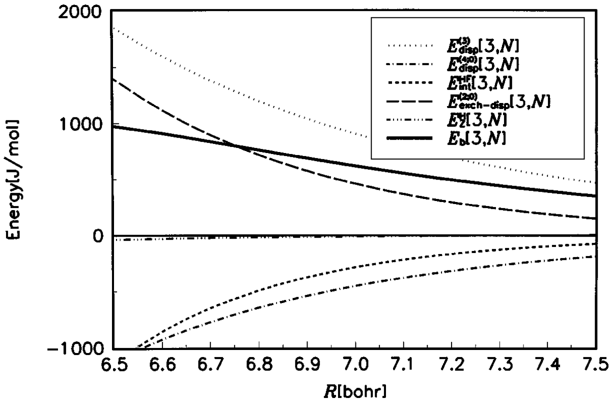

FIG. 2. Dependence of various nonadditive contributions to the binding energy of fcc argon on nearest neighbor distance. All components except for $E_Z^H$ are static energy contributions.

It has been estimated in Ref. [16] that the error of the SAPT three-body potential is of the order of 10%, which translates into 0.7% error in the cohesion energy. The two-body potential of Aziz [26] was fitted to a broad range of experimental data and predicts the most accurate spectroscopic data to about 0.1%. If this potential is replaced by the 1986 potential of Aziz and Slaman [13], the cohesion energy would change by about 0.5% and we would expect that the uncertainty resulting from the two-body component should not be larger than this value. Similar uncertainty could be contributed by the neglected four- and higher-body effects if one assumes geometric convergence of the many-body expansion. Other sources of inaccuracies should be much smaller so that the total inaccuracy of the present values could be estimated to be of the order of 1%.

The two-body potential of Aziz [26] predicts the hcp structure to be more stable than the fcc structure by 0.003%. Our three-body nonadditive contribution favors the fcc structure by about 0.01%, enough to overcome the preference for the hcp structure of the additive contribution. The total binding energies for fcc and hcp structures are $-7752.9$ and $-7752.1$ J/mol, respectively, 0.01% different. The only direct measurements of this difference were made near the melting point and were based on vapor pressure of dilute Ar-$O_2$ alloys [29]. It was found that the fcc structure should be more stable by $0.012 \pm 0.0027\%$. This value is very close to the result of the present work, despite the fact that the measurement was done at 81 K while the present computations correspond to 0 K. Although the inaccuracy of our cohesion energy is of the order of 1%, the residual errors in the fcc and hcp cohesion energies are likely to cancel to a large extent so that the 0.01% difference should be meaningful, at least up to the sign and order of magnitude. All nonadditive components favor the fcc structure except for the fourth-order dispersion energy which cancels the favoring contribution due to the third-order dispersion nonadditivity. Thus, one may say that the nonadditive exchange contributions to the binding energy (in particular the first-order exchange energy included in $E_{\rm int}^{\rm HF}[3,N]$) are responsible for the stability of the fcc structure, a situation first hypothesized by Jansen [7].

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[1] C. Tessier, A. Terlain, and Y. Larher, Physica (Amsterdam) **113A**, 286 (1982).
[2] K. F. Niebel and J. A. Venables, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic Press, New York, 1976), Vol. 1, Chap. 9.
[3] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).
[4] Y. Muto, Proc. Phys. Math. Soc. Jpn. **17**, 629 (1943).
[5] R. J. Bell, J. Phys. B **3**, 751 (1970); M. B. Doran and I. J. Zucker, J. Phys. C **4**, 307 (1971).
[6] S. F. O'Shea and W. J. Meath, Mol. Phys. **28**, 1431 (1974); **31**, 515 (1976).
[7] L. Jansen, Adv. Quantum Chem. **2**, 119 (1965).
[8] W. Kolos and A. Les, Int. J. Quantum Chem. **6**, 1101 (1972).
[9] M. Bulski and G. Chalasinski, J. Chem. Phys. **86**, 937 (1987).
[10] B. Jeziorski, M. Bulski, and L. Piela, Int. J. Quantum Chem. **10**, 281 (1976).
[11] M. Bulski and G. Chalasinski, Theor. Chim. Acta **56**, 199 (1980); Chem. Phys. Lett. **89**, 450 (1982).
[12] W. J. Meath and R. A. Aziz, Mol. Phys. **52**, 225 (1984); see also W. J. Meath and M. Koulis, J. Mol. Struct. (Theochem) **226**, 1 (1991).
[13] R. A. Aziz and M. J. Slaman, Mol. Phys. **58**, 679 (1986).
[14] W. L. Bade, J. Chem. Phys. **28**, 282 (1958).
[15] A. Lucas, Physica (Utrecht) **35**, 353 (1967); A. Huller, Z. Phys. **241**, 340 (1971).
[16] V. F. Lotrich and K. Szalewicz, J. Chem. Phys. **106**, 9688 (1997).
[17] C. Isenberg and C. Domb, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1965), p. 141.
[18] M. J. Elrod and R. J. Saykally, Chem. Rev. **94**, 1975 (1994).
[19] V. F. Lotrich and K. Szalewicz, J. Chem. Phys. **106**, 9668 (1997).
[20] J. Henkel, J. Chem. Phys. **23**, 681 (1955).
[21] C. G. Chell and I. J. Zucker, J. Phys. C **1**, 35 (1968).
[22] G. K. Horton, in *Rare Gas Solids* (Ref. [2]), Chap. 1.
[23] R. J. Bell and I. J. Zucker, in *Rare Gas Solids* (Ref. [2]), Chap. 2.
[24] C. Domb and L. Salter, Philos. Mag. **43**, 1083 (1952).
[25] C. Isenberg, Phys. Rev. **132**, 2427 (1963).
[26] R. A. Aziz, J. Chem. Phys. **99**, 4518 (1993).
[27] H. R. Glyde, J. Phys. C **3**, 810 (1970).
[28] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).
[29] T. Bricheno and J. A. Venables, J. Phys. C **9**, 4095 (1975).