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Convergence of the Møller-Plesset perturbation series for the fcc lattices of neon and argon

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Complete basis set limit calculations are carried out for the fcc lattices of solid neon and argon, using second- to fourth-order Møller-Plesset theory, MP2–MP4, and coupled-cluster calculations, CCSD(T), to describe electron correlation within a many-body expansion of the interaction potential up to third order. A correct description of the three-body Axilrod-Teller-Muto term for the solid state is only obtained from third order on in the many-body expansion of the correlation energy, correcting the severe underestimation of long-range three-body effects at the MP2 level of theory. MP4 shows good agreement with the CCSD(T) results, and the latter are in good agreement with experimental lattice constants, cohesive energies, and bulk moduli. However, with increasing pressures the convergence of the Møller-Plesset series deteriorates as the electronic band gap decreases, resulting in rather large deviations for the equation of state (pressure-volume dependence). For neon, however, the errors in the MP2 two- and three-body terms almost cancel, i.e., at a volume of $V=3\ \mathrm{cm^3/mol}$ the MP2 pressure is underestimated by only 1 GPa compared to the pressure of $P=251$ GPa calculated at the CCSD(T) level of theory. In contrast, for argon this is not the case, and at $V=5.5\ \mathrm{cm^3/mol}$ the calculated MP2 pressure of 228 GPa deviates substantially from the CCSD(T) result of 252 GPa.

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I. INTRODUCTION

Quantum theoretical methods for electronic-structure theory have advanced rapidly in the past 20 years. This is nicely demonstrated by the Fock-spaced coupled cluster calculations for atoms carried out in Kaldor's group,[1,2] which for ionization potentials and electron affinities reach accuracies on the order of a few millielectron volts even for the heaviest elements in the periodic table where one needs to include both relativistic and quantum electrodynamic effects.[3,4] High accuracies are also achieved in molecular structure calculations as demonstrated recently for a set of small molecules by Helgaker *et al.*,[5] Klopper *et al.*,[6] or Stanton and co-workers.[7] The situation changes completely if one considers the solid state. Here, one mainly relies on density-functional theory, which, unlike wave-function-based methods, is difficult to be improved systematically toward the exact result.[8] However, in the last few years post-Hartree-Fock (HF) and Kohn-Sham methods for electron correlation based on wave-function theory were introduced in computational solid-state physics; most noteworthy are the local second-order Møller-Plesset many-body perturbation theory (LMP2) by Pisani *et al.*,[9–11] and the random-phase approximation (RPA) by Kresse, Scuseria, and co-workers.[12–14] The former has the advantage that it is computationally affordable but is only applicable to solids with large band gaps (insulators) to ensure the convergence of the Møller-Plesset series MPn with increasing order n,[10] i.e., it cannot be used to describe small or zero band-gap materials such as metallic systems where the energy difference in the denominator of the many-body series approaches zero. The RPA avoids this but is computationally far more demanding. A completely different approach is the use of the incremental method developed by Stoll and co-workers,[15–18] where the correlation energy of the solid is expanded in terms of localized orbitals at different atomic centers.[17] Stoll's method of increments, if carried out at the coupled cluster level of theory, can successfully be applied to a variety of electronic systems even for solids with small band gaps and metallic systems.[19–24] More recent developments include explicitly correlated MP2 (MP2-R12 and MP2-F12) for infinite systems by Shiozaki and Hirata.[25]

While dispersion interactions between atoms in small molecules are well understood and studied, a detailed analysis for the solid state is still missing. Especially if the solid is put under high pressure, both short- and long-range interactions become important.[26] In a previous paper we showed that the incorrect description of three-body Axilrod-Teller-Muto[27,28] type of interactions by second-order Møller-Plesset theory for electron correlation leads to significant errors for the rare gas solid-state structures.[29] The importance of such nonadditive forces is well known and has already been described in the literature for weakly interacting molecules,[30,31] as well as for the liquid and solid state.[32–35] Here we mention the work by Chałasiński and co-workers who analyzed in detail the many-body contributions in weakly interacting atoms and molecules.[30,36–38] It is however not clear how well the Møller-Plesset expansion MPn with increasing order n converges for the solid state, as, for example, the number of three-body (Axilrod-Teller-Muto) terms in the energy decomposition increases quadratically with increasing number of atoms compared to a linear scaling for the two-body terms, and therefore three-body effects become quite important.[39–41] We point out that the convergence of the Møller-Plesset series has been studied extensively for atomic and molecular systems in the past[42–46] including weakly interacting systems,[30] and it is well understood that the convergence radius critically depends on the band gap (highest occupied molecular orbital-lowest unoccupied molecular orbital gap in atoms and molecules).[46–48]

The rare gas solids represent ideal test cases for the performance of the Møller-Plesset series expansion, as the band gap is large and the total energy of the lattice can be easily expanded into a many-body series of the interaction potential.[41] Moreover, one can expect similar results for other weakly interacting systems found, for example, in molecular crystals.[49] We therefore investigate the convergence of the Møller-Plesset series for the fcc crystals of neon and argon up to fourth order in the electron correlation energy, and compare our results to more accurate coupled cluster calculations. It is well known that the convergence toward the basis set limit is much slower for wave-function-based methods than for density-functional theory, as it is difficult to correctly describe the electron-electron cusp. Therefore, in order to avoid basis set effects we estimated the complete basis set (CBS) limit at each level of theory. Further, the performance of the Møller-Plesset series was investigated for the equation of state (pressure-volume relation) at 0 K, as three-body interactions become very important at high pressures.[50]

II. COMPUTATIONAL DETAILS

The cohesive energy per atom, E_{coh}, for the face-centered-cubic structures of solid neon and argon was obtained from a many-body expansion of the interaction potential utilizing translational symmetry,[41]

$$E_{coh}(V) = \sum_{k=2}^{\infty} E^{(k)}(V)$$

$$\cong \frac{1}{2}\sum_{i=1}^{N_1} E^{(2)}(r_{0i}) + \frac{1}{3}\sum_{i=1}^{N_1}\sum_{j>i}^{N_2} E^{(3)}(r_{0i},r_{0j},r_{ij}) + \cdots, \tag{1}$$

where r_{0i} is the distance between the inner most (central) atom and atom i in the fcc lattice. V is the volume of the fcc unit cell with $V_{\mathrm{fcc}}=a^3/4$ and a being the fcc lattice constant. We truncated the series expansion at $k=3$, as four-body forces are rather small around the equilibrium lattice constant, and the errors introduced by this truncation are within the errors of the other approximations applied. The cluster size N_1 for the fcc lattice was set to 60 000 atoms, sufficiently large to achieve convergence of the optimized lattice constant to 0.1 mÅ for the two-body interaction (the exact two-body limit is obtained from the extended Lennard-Jones form as discussed below).[41,51] As the three-body term is about one order of magnitude smaller than the corresponding two-body term and decays faster with increased interatomic distances, we can restrict N_2 to $N_2=25\,000$. It was pointed out before that the (formally exact) many-body expansion Eq. (1) converges fast for the rare gas crystals, even at higher pressures.[41,50,52]

The two-body ($E^{(2)}$) and three-body ($E^{(3)}$) interaction energies in Eq. (1) for neon and argon were obtained pointwise from nonrelativistic second-(MP2), third-(MP3), and complete fourth-order (MP4) Møller-Plesset calculations, as well as coupled cluster calculations with single and double substitutions, CCSD, and including perturbative triples, CCSD(T),[53] utilizing the frozen-core approximation by keeping only the occupied valence *nsp*-space active. We used a large range of atomic distances r between 1.7 and 6.0 Å (2.2 and 8.0 Å) to sample the potential-energy surfaces for the dimers and trimers (in equilateral triangle shape) of neon (argon). All-electron augmented correlation consistent aug-cc-pVnZ basis sets (with cardinal number $n=2-5$) (Refs. 54–57) were used to study the basis set convergence with increasing size, and the extrapolation scheme of Halkier *et al.*[58] for the electron correlation energy E^c was used to obtain the complete basis set limit from the $n=4$ and $n=5$ basis set results, according to

$$E^c(n) = E^c(\mathrm{CBS}) + \beta n^{-3}. \tag{2}$$

We note that the HF energy $E_{\mathrm{HF}}(n)$ is practically converged for $n=5$ and was taken as the HF basis set limit $E_{\mathrm{HF}}(\mathrm{CBS})$. All calculated interaction energies were corrected for basis set superposition errors (BSSEs) according to the Boys-Bernardi method,[59]

$$E_X^{(2)}(r) = E_{XX}(r) - 2E_{XG}(r), \tag{3}$$

$$E_X^{(3)}(r) = E_{XXX}(r) - 3E_{XXG}(r) + 3E_{XGG}(r). \tag{4}$$

Here, X denotes the rare gas element and G the presence of a ghost atom basis set(s) at position(s) otherwise occupied by atom X. In order to apply these two-body and three-body interaction energies to the solid state according to Eq. (1), we fitted $E^{(2)}(r)$ to an extended Lennard-Jones potential as described in detail in Ref. 41,

$$E_X^{(2)}(r_{ij}) = \sum_{m=6}^{20} C_m r_{ij}^{-m}, \quad \text{with} \quad r_{ij} > r_{min}. \tag{5}$$

This ansatz has the advantage that the cohesive energy can be obtained analytically from the Lennard-Jones-Ingham coefficients.[41,60] Furthermore, the fit is usually smooth up to higher derivatives in $E_X^{(2)}(r_{ij})$ for $r_{ij}>r_{min}$, and the least-squares fits give root-mean-square errors which are as small as for the more sophisticated diatomic potential curves used to describe the whole interaction range.[61] $E^{(3)}(r)$ is approximated by an extended Axilrod-Teller-Muto potential that accounts for both the attraction in the overlap region and the repulsion in the long-range part,[50]

$$E_X^{(3)}(r_{ij},r_{jk},r_{ik}) = f_\theta\left(C_{AT} r_g^{-9} + e^{-\alpha r_s}\sum_{n=0}^{5} A_{2n} r_g^{2n}\right),$$

with

$$f_\theta = (1 + 3\cos\theta_i \cos\theta_j \cos\theta_k),$$

$$r_g = (r_{ij} r_{jk} r_{ik})^{1/3}, \quad \text{and} \quad r_s = r_{ij} + r_{jk} + r_{ik} \tag{6}$$

and we have $r_{ij} > r_{min}$ for each $i \neq j$. The adjusted coefficients from the potential energy fits are listed in Table I. Here we note that the functional form used is an extension to the

TABLE I. Coefficients for the two- and three-body potentials for neon and argon as defined in Eqs. (5) and (6). All distances in Å and energies in atomic units.

Coefficients	MP2	MP3	MP4	CCSD	CCSD(T)
Neon two-body					
C_6	-1.41955×10^{-1}	-1.48074×10^{-1}	-1.75480×10^{-1}	-1.45210×10^{-1}	-1.67341×10^{-1}
C_8	-4.87134×10^{0}	-3.54939×10^{0}	-3.46512×10^{0}	-5.32456×10^{0}	-5.20790×10^{0}
C_9	9.43441×10^{1}	7.80539×10^{1}	8.48474×10^{1}	9.81993×10^{1}	1.00349×10^{2}
C_{10}	-4.59290×10^{2}	-3.93557×10^{2}	-4.46742×10^{2}	-4.70897×10^{2}	-4.90939×10^{2}
C_{12}	3.44798×10^{3}	2.93618×10^{3}	3.52902×10^{3}	3.46444×10^{3}	3.67621×10^{3}
C_{14}	-1.70325×10^{4}	-1.38105×10^{4}	-1.78336×10^{4}	-1.68745×10^{4}	-1.82001×10^{4}
C_{16}	4.73043×10^{4}	3.57615×10^{4}	5.06155×10^{4}	4.63325×10^{4}	5.09539×10^{4}
C_{18}	-6.98364×10^{4}	-4.83908×10^{4}	-7.65950×10^{4}	-6.77537×10^{4}	-7.62121×10^{4}
C_{20}	4.28769×10^{4}	2.67674×10^{4}	4.83673×10^{4}	4.12736×10^{4}	4.76084×10^{4}
Neon three-body					
C_{AT}	1.47149×10^{-4}	2.90448×10^{-2}	3.26249×10^{-2}	3.37596×10^{-2}	4.06612×10^{-2}
A_0	-5.95000×10^{2}	-5.67817×10^{2}	-5.03308×10^{2}	-4.74995×10^{2}	-4.80005×10^{2}
A_2	-4.31498×10^{2}	8.31106×10^{1}	5.32026×10^{0}	3.04482×10^{1}	1.91417×10^{1}
A_4	-2.64281×10^{2}	-1.99706×10^{2}	-1.54846×10^{2}	-1.39810×10^{2}	-1.42856×10^{2}
A_6	-6.95825×10^{1}	3.36711×10^{1}	2.23213×10^{1}	2.40420×10^{1}	2.39623×10^{1}
A_8	6.41023×10^{0}	-2.06120×10^{0}	-7.55803×10^{-1}	-1.34529×10^{0}	-1.10469×10^{0}
A_{10}	1.24831×10^{-1}	7.63010×10^{-2}	2.21240×10^{-2}	3.81317×10^{-2}	2.36032×10^{-2}
α	2.69379×10^{0}	2.42644×10^{0}	2.41860×10^{0}	2.38005×10^{0}	2.38939×10^{0}
Argon two-body					
C_6	-1.95388×10^{0}	-1.54323×10^{0}	-1.75567×10^{0}	-1.44901×10^{0}	-1.71568×10^{0}
C_8	-8.52074×10^{1}	-7.62721×10^{1}	-8.24211×10^{1}	-7.45489×10^{1}	-8.23259×10^{1}
C_9	2.03725×10^{3}	1.86985×10^{3}	2.02560×10^{3}	1.79898×10^{3}	2.02006×10^{3}
C_{10}	-1.23063×10^{4}	-1.13920×10^{4}	-1.23765×10^{4}	-1.08935×10^{4}	-1.23340×10^{4}
C_{12}	1.35546×10^{5}	1.24247×10^{5}	1.36858×10^{5}	1.18323×10^{5}	1.36251×10^{5}
C_{14}	-9.34500×10^{5}	-8.14246×10^{5}	-9.37814×10^{5}	-7.65316×10^{5}	-9.31340×10^{5}
C_{16}	3.26447×10^{6}	2.49098×10^{6}	3.21338×10^{6}	2.25294×10^{6}	3.17164×10^{6}
C_{18}	-4.87508×10^{6}	-2.24505×10^{6}	-4.51433×10^{6}	-1.61706×10^{6}	-4.37048×10^{6}
C_{20}	1.26291×10^{6}	-2.34952×10^{6}	5.86474×10^{5}	-3.04279×10^{6}	3.85056×10^{5}
Argon three-body					
C_{AT}	3.00245×10^{-2}	2.29722×10^{0}	1.56113×10^{0}	1.49059×10^{0}	1.75277×10^{0}
A_0	2.52739×10^{3}	-2.82581×10^{1}	1.36850×10^{3}	1.27837×10^{3}	1.34605×10^{3}
A_2	-3.56109×10^{3}	-1.56516×10^{3}	-2.71001×10^{3}	-2.58484×10^{3}	-2.61699×10^{3}
A_4	-1.15254×10^{2}	5.44492×10^{1}	5.09201×10^{2}	4.30313×10^{2}	4.95611×10^{2}
A_6	-1.54501×10^{2}	-1.18081×10^{2}	-1.90652×10^{2}	-1.80012×10^{2}	-1.80895×10^{2}
A_8	-3.55054×10^{1}	6.91333×10^{0}	1.51729×10^{1}	1.28848×10^{1}	1.49800×10^{1}
A_{10}	3.36983×10^{0}	1.56867×10^{-1}	-2.67911×10^{-1}	-1.56480×10^{-1}	-2.87608×10^{-1}
α	2.27521×10^{0}	2.10135×10^{0}	2.08460×10^{0}	2.09698×10^{0}	2.07328×10^{0}

three-body potential proposed by Bruch and McGee,[62] which has been used successfully by Loubeyre for dense helium[63] as well as Freiman and Tretyak for the dense solid rare gases He, Ne, Ar, Kr, and Xe.[64] In the fit procedure we used $r_{min}=1.7$ Å for neon and 2.2 Å for argon, which assures the applicability of the potential curves up to pressures of about 200 GPa. The power expansions in both Eqs. (5) and (6) have been extended in comparison to Ref. 50 to achieve best possible fits at small interatomic distances, i.e., at high pressures. First, we fitted the long-range part of the potential curve to $C_6 r^{-6}$ to correctly describe this region, then by keeping C_6 fixed we adjusted all other parameters. This gives CCSD(T) C_6 parameters for neon (−6.74 a.u.) and argon (−78.1 a.u.) in good agreement with the values listed by

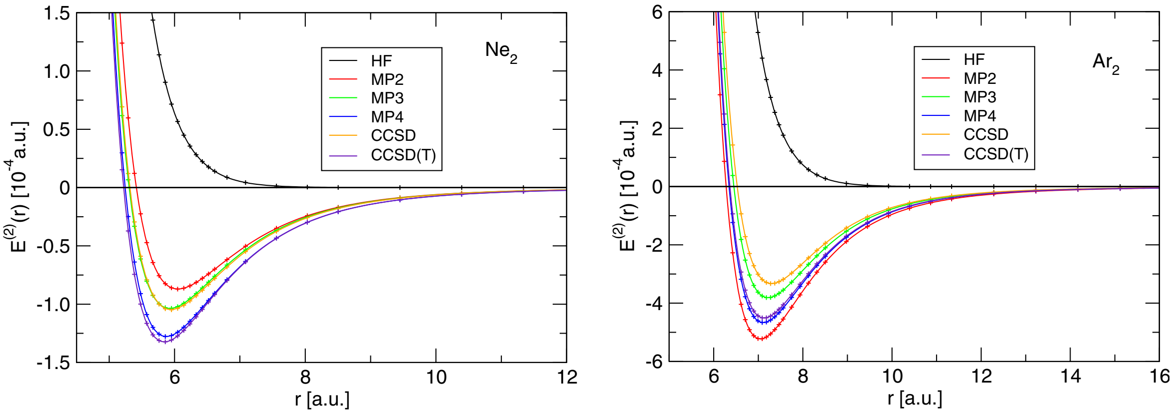

FIG. 1. (Color online) Two-body potential curves for Ne$_2$ and Ar$_2$ at various levels of theory from CBS limit calculations.

Barker in 1976 (−6.43 a.u. and −64.2 a.u., respectively),[65] or the more recent values by Kumar and Thakkar (−6.35 a.u. and −64.42 a.u., respectively).[31] Note that the other C_i need to describe both the short and medium to long-range part and cannot be compared to the long-range dispersion coefficients. Moreover, for the very high-pressure range ($P > 100$ GPa) the extended Lennard-Jones fit becomes numerically rather unstable (as do other functional forms because of the very large energies involved), and we used a different set of fit parameters for this range to describe this region more accurately. We also mention that in order to describe both the extreme short- and long-range regions correctly, one could also apply more sophisticated potential forms like the Tang-Toennies potential function,[66] used, for example, for neon and argon by Vogel and co-workers.[67,68] However, the extended Lennard-Jones potential is computationally more efficient and is sufficient to discuss the convergence of the Møller-Plesset perturbation series here.

Spectroscopic constants for the dimeric neon and argon molecules were obtained using the numerical Numerov-Cooley procedure.[69,70] Zero-point vibrational effects (E_0) to the cohesive energy of the fcc lattice were obtained from the Einstein approximation,[71] and anharmonicity effects are included within this approximation using perturbation theory as described in detail in Refs. 41 and 72.

III. RESULTS AND DISCUSSION

A. Two-body interactions

The diatomic potential curves are shown in Fig. 1 and the spectroscopic constants obtained from these curves are listed in Table II. Figure 1 illustrates that for the rare gas dimers only MP4 closely resembles the CCSD(T) results, MP2 underestimates the binding energy for Ne$_2$ and overestimates it for Ar$_2$ (see also discussion in Ref. 77). The perturbative triple contributions in the coupled cluster procedure are important and should not be neglected. This is also reflected in the spectroscopic constants. At the CCSD(T) level of theory the spectroscopic constants are in good agreement with experimental results, despite the fact that, for example, relativistic effects are neglected for argon. Note that the experimental harmonic frequencies and anharmonicity constants carry large uncertainties, as only very few vibrational levels fit into these potential-energy curves. Regarding the hard-sphere radius r_c, defined as the onset of the repulsive wall between two atoms, for Ne$_2$ the MP2 value is too large by about 0.10 Å, and for Ar$_2$ it is too small by about 0.04 Å compared to our CCSD(T) result. This implies that the repulsion is overestimated for neon as the repulsive region is entered at too large interatomic distances but underestimated for argon, which, as we shall see, has important consequences for the accurate determination of the pressure-volume relation in the condensed state. We note that our CCSD(T) results are in good agreement with the most precise relativistic coupled cluster calculations for the neon and argon dimers by Vogel and co-workers, who obtained equilibrium bond distances of 3.089 Å for Ne$_2$ and 3.762 Å for Ar$_2$, and hard sphere radii of 2.761 Å and 3.357 Å, respectively.[67,68]

B. Three-body interactions

The three-body potential curves for Ne$_3$ and Ar$_3$, for ideal D_{3h} symmetry trimers (equilateral triangle), are shown in Fig. 2. Similar to HF, MP2 cannot describe the correct long-range Axilrod-Teller-Muto behavior. In fact, the energy at the maximum of the three-body potential curve is underestimated by more than two orders of magnitude for neon and one order of magnitude for argon. This is reflected in the MP2 values of the long-range three-body coefficients C_{AT}, which are far too small compared to the CCSD(T) result, as pointed out before.[29] At the CCSD(T) level of theory the C_{AT} coefficients are in rather good agreement with the estimated values by Barker,[65] their values being $C_{AT}=12.0$ a.u for neon and 517.3 a.u. (our results converted to atomic units are 12.6 and 531.1, respectively). Our values also compare well with more recent data by Kumar and Thakkar (11.92 a.u. and 519.0 a.u. for Ne and Ar, respectively).[31]

A significant improvement toward the more accurate coupled-cluster results is obtained when using MP3. Here, we note that the three-body Axilrod-Teller-Muto term arises from the coupling of all three pair interactions (triple dipole term) in a perturbation series with a zero-order Hamiltonian that consists of the exact spectrum of the three noninteracting atoms.[78] Although the Møller-Plesset series starts differently from the Hartree-Fock operator as the zero-order Hamil-

TABLE II. Calculated spectroscopic constants for Ne_2 and Ar_2 in comparison with experimental results. Equilibrium bond distances r_e in Å, binding energy D_e, dissociation energy D_0 (corrected for zero-point vibration), harmonic frequency ω_e, and anharmonicity constant $\omega_e x_e$, all in cm^{-1}. The two-body hard-sphere radius r_c (Å) defined by $E^{(2)}(r_c)=0$, the three-body potential maximum position r_m (Å) and corresponding energy $E^{(3)}(r_m)$ (cm^{-1}), and the radius r_0 (Å) where the three-body potential becomes attractive as defined by $E^{(3)}(r_0)=0$ are also listed. Experimental values are taken from Refs. 73–76.

Atom	Property	MP2	MP3	MP4	CCSD	CCSD(T)	Expt.
				Two-body			
Neon	r_e	3.202	3.136	3.107	3.144	3.093	3.094 ± 0.001
	r_c	2.866	2.807	2.775	2.813	2.763	
	D_e	19.1	22.7	28.0	23.0	29.0	29.4 ± 0.012
	D_0	9.5	11.9	15.9	12.2	16.6	16.8
	ω_e	22.6	25.2	27.9	25.2	28.6	28.9[a]
	$\omega_e x_e$	6.9	7.3	7.3	7.2	7.4	7.6[a]
Argon	r_e	3.729	3.819	3.762	3.861	3.772	3.761(3)
	r_c	3.323	3.414	3.357	3.454	3.367	
	D_e	114.5	83.4	102.1	72.9	98.7	99.2
	D_0	98.2	69.4	86.7	59.9	83.5	84.8
	ω_e	34.0	29.8	32.6	27.5	32.1	31.4
	$\omega_e x_e$	3.2	3.5	3.3	3.4	3.4	2.9
				Three-body			
Neon	r_m	3.609	2.959	2.943	2.960	2.892	
	r_0	3.455	2.756	2.741	2.755	2.690	
	$E^{(3)}(r_m)$	0.0021	0.406	0.475	0.438	0.647	
Argon	r_m	3.968	3.503	3.640	3.682	3.595	
	r_0	3.756	3.239	3.380	3.419	3.335	
	$E^{(3)}(r_m)$	0.24	6.50	3.01	2.57	3.75	

[a]These values are based on only two vibrational levels reported in Ref. 73.

tonian, it is clear that the long-range behavior is dominated by electron correlation, and the Axilrod-Teller-Muto term can only be described satisfactorily by third-order Møller-Plesset theory, which couples all double substitutions.[79] This was correctly pointed out by Chałasiński and co-workers who gave a detailed analysis of weak interactions in terms of both the order in the Møller-Plesset expansion and the interaction potential.[80] In fact, Chałasiński *et al.* pointed out that the *n*-body dispersion nonadditivity appears no sooner than in the *n*th order in the Rayleigh-Schrödinger perturbation expansion of the correlation energy.[30,81] Nevertheless, Fig. 2 shows that it is by far more difficult to describe the repulsive part of the three-body interaction correctly, and even the MP4 curves deviate significantly from CCSD(T) for both

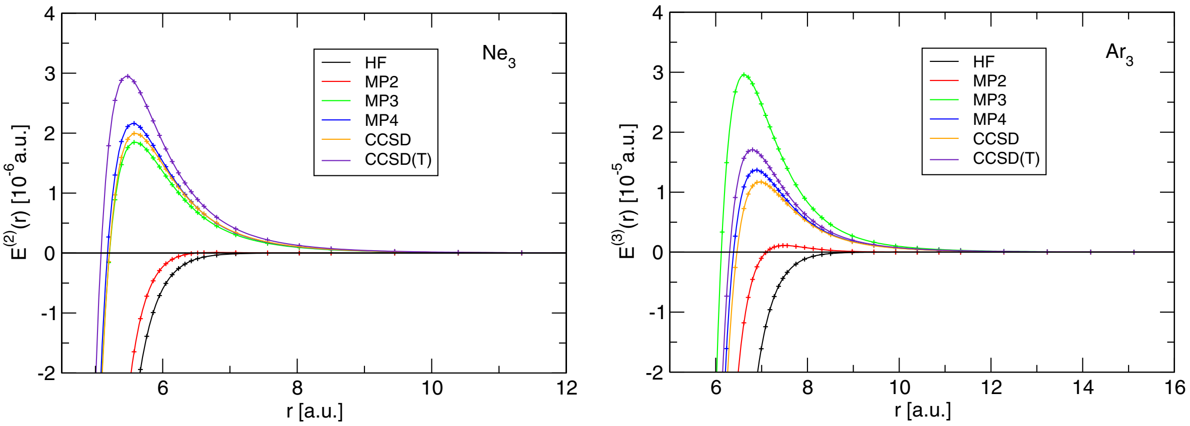

FIG. 2. (Color online) Three-body potential curves for the equilateral triangle of Ne_3 and Ar_3 at various levels of theory from CBS limit calculations.

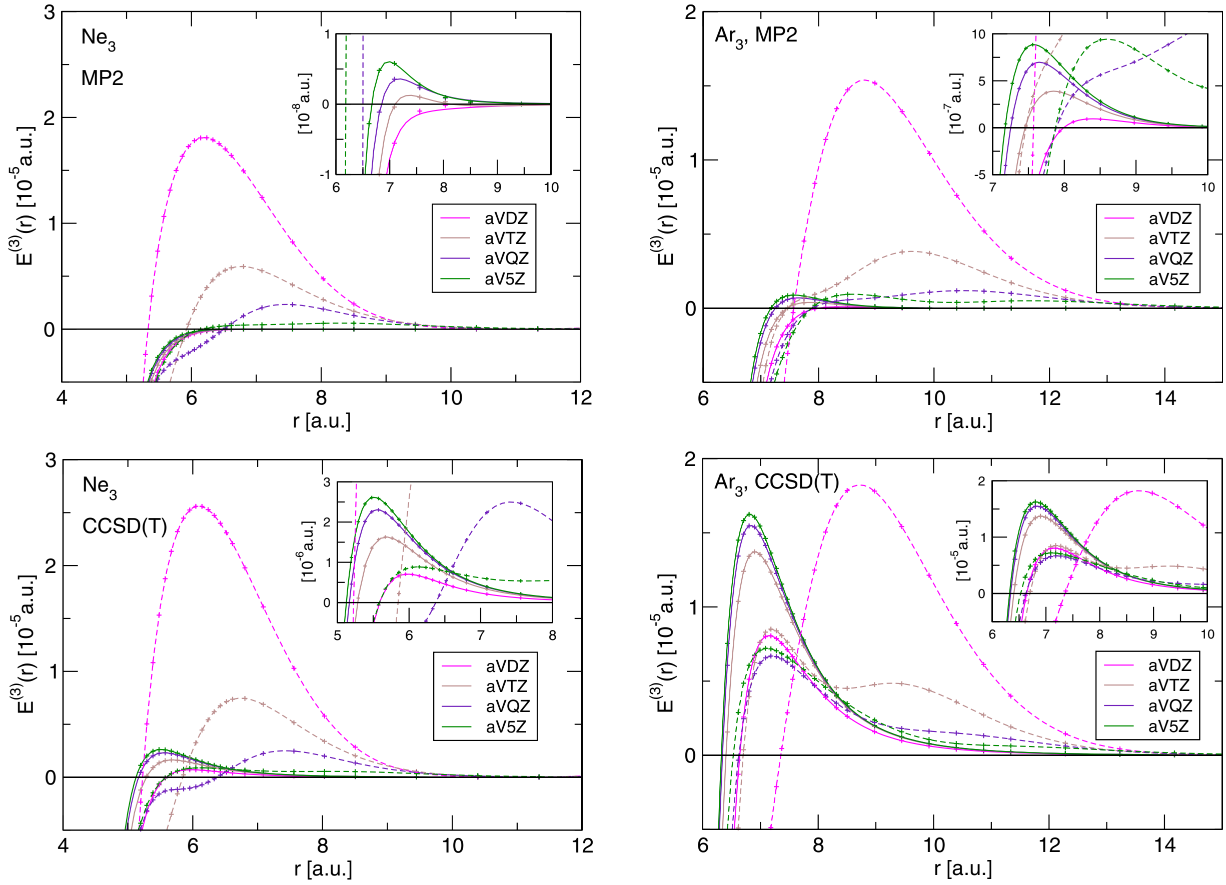

FIG. 3. (Color online) Basis set dependence of the three-body potential curves for the equilateral triangle of Ne_3 (left) and Ar_3 (right) from aug-ccPVnZ (abbreviated as aVnZ) MP2 (top) and CCSD(T) (bottom) calculations. Solid lines: including counterpoise correction; dashed lines: without counterpoise correction. Inlets highlight details in important regions.

neon and argon, and perhaps higher order coupled cluster calculations are also required to obtain more accurate results in this region, as, for example, done recently by Vogel and co-workers.[67,68] Moreover, as the slopes of the three-body curves are quite different in the attractive region, with MP2 mostly affected by this, we expect larger deviations in the high-pressure range (strong overlap region) for the equation of state (pressure-volume relation).

To illustrate the importance of correcting for the BSSE in the three-body potential, we show the uncorrected curves in Fig. 3 for various aug-ccPVnZ basis sets. For several basis sets, we obtain an erratic functional behavior for $E^{(3)}(r)$, not seen in the BSSE-corrected potentials. Moreover, if not corrected for BSSE the smaller basis sets can overestimate long-range interactions by orders of magnitude. Hence, the BSSE becomes crucially important for the three-body term, even more so than for the two-body interaction.

C. Solid-state calculations

The results of our solid-state calculations are summarized in Table III. The CCSD(T) results are in very good agreement with the experimental values if zero-point vibrational effects are included in the lattice optimization. Such effects become quite important for both neon and argon, i.e., without the inclusion of zero-point vibrational effects one cannot accurately reproduce the experimental values for these solid-state properties. We note that the anharmonic contribution to the cohesive energy of neon at the CCSD(T) optimized lattice constant is $-4.8\ \text{cm}^{-1}$ compared to the much larger harmonic term of $-48.1\ \text{cm}^{-1}$. The latter in turn is much larger than the three-body contribution to the cohesive energy of $-5.8\ \text{cm}^{-1}$ (the two-body contribution is $215.7\ \text{cm}^{-1}$). The CCSD(T) bulk modulus for neon is in excellent agreement with experiment. Here, we note that even the anharmonic vibrational contributions become important, i.e., at the optimized CCSD(T) lattice constant we obtain from the two-body term $B=6.1$ kbar; including the three-body contribution adds $\Delta B=0.4$ kbar, the contribution from the harmonic zero-point vibrations is $\Delta B=4.0$ kbar, and the anharmonic corrections to the zero-point vibrational term add another $\Delta B=0.5$ kbar. Equally large vibrational effects are calculated for argon.

As noted earlier, MP2 overestimates the binding strength for argon but underestimates it for neon. This is partially compensated at the MP3 level of theory but only MP4 gives results comparable with experimental data or CCSD(T). The convergence behavior of the Møller-Plesset series in the two-body lattice constants a, cohesive energies E_{coh}, and bulk moduli B for both neon and argon is reflected in the convergence behavior of the corresponding dimer bond distances r_e, binding energies D_e, and vibrational frequencies ω_e (the lat-

TABLE III. Calculated lattice parameters a (Å), cohesive energies E_{coh} (cm^{-1}), and bulk moduli B (kbar) for the rare gas fcc solids of neon and argon. Experimental values are taken from Refs. 82–87.

Prop.	Method	MP2	MP3	MP4	CCSD	CCSD(T)	Expt.
				Neon			
a	$E^{(2)}$	4.436	4.346	4.301	4.356	4.286	
	$E^{(2)}+E^{(3)}$	4.429	4.357	4.311	4.368	4.300	
	$E^{(2)}+E^{(3)}+E_0$	4.641	4.553	4.487	4.563	4.474	4.464
E_{coh}	$E^{(2)}$	150.6	178.5	221.0	180.5	224.7	
	$E^{(2)}+E^{(3)}$	151.2	173.4	214.8	174.9	216.8	
	$E^{(2)}+E^{(3)}+E_0$	99.7	117.7	152.5	119.2	154.0	161.6
B	$E^{(2)}$	12.2	15.4	19.0	15.4	19.6	
	$E^{(2)}+E^{(3)}$	12.1	14.6	18.1	14.6	18.5	
	$E^{(2)}+E^{(3)}+E_0$	6.5	8.2	10.5	8.2	10.8	11.0
				Argon			
a	$E^{(2)}$	5.160	5.296	5.212	5.354	5.227	
	$E^{(2)}+E^{(3)}$	5.142	5.353	5.234	5.383	5.258	
	$E^{(2)}+E^{(3)}+E_0$	5.200	5.425	5.298	5.459	5.322	5.300
E_{coh}	$E^{(2)}$	898.0	643.7	792.2	562.4	764.5	
	$E^{(2)}+E^{(3)}$	901.3	576.0	746.0	526.4	712.0	
	$E^{(2)}+E^{(3)}+E_0$	818.9	514.8	673.6	466.8	641.9	645.5
B	$E^{(2)}$	43.4	30.5	38.2	26.0	36.7	
	$E^{(2)}+E^{(3)}$	42.0	25.7	34.3	23.3	32.6	
	$E^{(2)}+E^{(3)}+E_0$	36.1	21.2	29.0	19.1	27.4	26.7

ter through $B \propto \omega_e^2/r_e$). These relationships can be derived from ideal Lennard-Jones type of interactions and were discussed in detail in Ref. 41. The non-negligible three-body effects and zero-point vibrational corrections for the bulk properties significantly change these values but do not change the overall trend in the MPn convergence with increasing n, which is obviously dominated by the two-body part.

We briefly discuss four-body effects, which are not included here as they are expected to be one order of magnitude smaller than the three-body contributions at normal pressure.[81] Rościszewski *et al.* estimated four-body effects for the rare gas solids using an incremental scheme for electron correlation.[40] For neon these effects are rather small, i.e., the lattice constant is increased by only 0.001 Å, the cohesive energy increases by 0.7 cm^{-1} and there is basically no change in the bulk modulus.[40] However, for argon four-body terms in the interaction potential are slightly more important. Here, the lattice constant is increased by only 0.002 Å, the cohesive energy by 5.5 cm^{-1} and the bulk modulus is decreased by 0.5 kbar.[40] Nevertheless, these effects are within all other errors in our approximations applied, and therefore the neglect of higher order terms in the interaction potential is justified.

D. Møller-Plesset convergence at high pressures

For neon and argon the pressure-volume curves at different temperatures are well known experimentally up to relatively high pressures,[81,88–94] and will not be discussed here (for neon a detailed discussion has been provided in Ref. 50). Here, we concentrate on the performance of the Møller-Plesset perturbation series as compared to the more accurate coupled cluster results.

It is well known that the MPn series starts to diverge with decreasing electronic band gap. Figure 4 shows the electronic $^1\Sigma_g^+ \rightarrow {}^3\Sigma_u^+$ transition energy with varying bond distance for the neon and argon dimers. As the dimers interact only weakly, the CCSD(T) results for the singlet-triplet gaps at the respective equilibrium distances of the neon (16.79

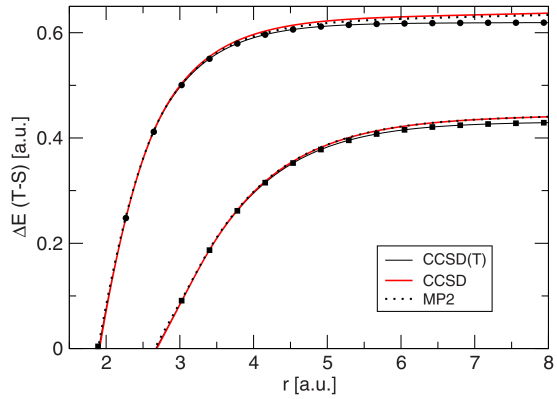

FIG. 4. (Color online) The singlet-triplet gap for Ne$_2$ (upper curves) and Ar$_2$ (lower curves) obtained from separate SCF calculations for the two states at various levels of theory using an aug-ccpVTZ (+three diffuse s functions) basis set.

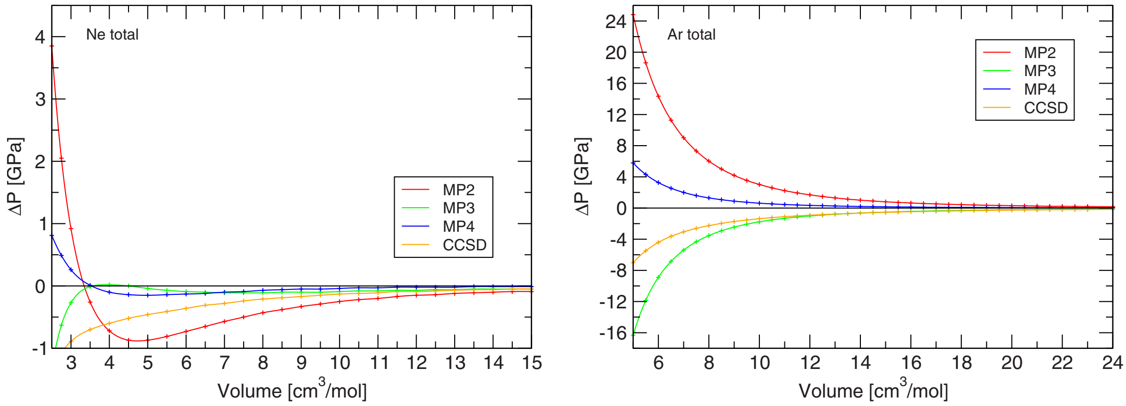

FIG. 5. (Color online) Deviation of the calculated pressure from the CCSD(T) result, i.e., $\Delta P = P_{\mathrm{CCSD(T)}} - P_M$, where M stands for MP2, MP3, MP4, and CCSD.

eV) and argon dimers (11.60 eV) are not too different from the $^1S_0 \rightarrow {}^3P_2$ transitions of atomic neon [our CCSD(T) value 16.55 eV; exp. 16.62 eV (Ref. 95)] and argon [CCSD(T) 11.45 eV; exp. 11.55 eV (Ref. 95)]. In fact, this slight increase compared to the atomic values is caused by the perturbative triple corrections in the coupled cluster procedure and might disappear if such contributions are treated variationally. Nevertheless, at smaller distances the gap between the antibonding occupied np and the bonding unoccupied $(n+1)s$ orbitals becomes smaller with decreasing interatomic distance. Another important fact is that the Møller-Plesset curves follow closely the CCSD(T) results down to shorter bond distances [the MP3 and MP4 curves follow closely the CCSD(T) curve shown in Fig. 4]. At very short distances, i.e., around 1.01 Å for neon and 1.42 Å for argon, the triplet state falls below the singlet state, i.e., there is a curve crossing between the two states in the repulsive region. However, such small distances in solid neon and argon translate into volumes of 0.43 $\mathrm{cm}^3/\mathrm{mol}$ for Ne and 1.21 $\mathrm{cm}^3/\mathrm{mol}$ for Ar, and therefore into extremely high pressures beyond the terapascal range. Even though the closure of the band gap in the solid state is expected to occur at larger internuclear distances when compared to the dimer, we do not expect observation of the band gap closure within a pressure range accessible in laboratory experiments. For example, the band-gap closure in solid helium is expected at around 26 TPa.[96] Only for dense helium at temperatures of 60 000 K conductivity has been observed recently using laser-driven shock wave techniques in a diamond-anvil cell.[97] The optical spectra for neon and argon at high pressures are not known, and a metallic phase transition has yet to be observed for neon and argon at low temperatures. For xenon the gap is small enough for the metallic phase transition to be observed at pressures of 150 GPa.[98] Nevertheless, preliminary gradient-corrected density-functional calculations show that the single-particle gap for solid argon closes at a nearest-neighbor distance of 2.15 Å (volume density 4.25 $\mathrm{cm}^3/\mathrm{mol}$), as expected larger than the calculated dimer distance for singlet-triplet gap closure. We mention that the experimentally determined band gap in solid neon at normal pressure is surprisingly high at 21.69 eV,[99,100] and that of solid argon is 14.3 eV.[101] Both values are in fact close to the experimental atomic ionization potentials for neon (21.56 eV) and argon (15.76 eV),[95] which suggests that the band gap for the solids may require some reevaluation.

As the rare gas solids are wide-gap insulators up to high pressures, we expect that neon and argon are well described by Møller-Plesset perturbation theory up to pressures accessible in the laboratory (i.e., to about 250 GPa). This is indeed the case as depicted in Fig. 5, i.e., the deviation of the calculated MP4 pressure from CCSD(T) results is rather small up to relatively small volumes (high pressures of $P \approx 100$ GPa). However, it is also clear that the deviations of the MPn series from the CCSD(T) calculated pressures become larger with decreasing volume (increasing pressure), and at very small volumes we see that the MPn series starts to diverge. We note however, that even under huge compression the MP2 pressure deviates by less than 10% from the CCSD(T) result for both neon and argon. It is also evident that neon and argon show quite different behavior in the pressure deviations, which we analyze in more detail.

At a volume of $V=3$ $\mathrm{cm}^3/\mathrm{mol}$ for neon, the MP2 result for the solid underestimates the CCSD(T) calculated total pressure (approximately 251 GPa) by only 1 GPa, whereas the deviations are much larger for argon in that pressure range [$\Delta P=24$ GPa between MP2 and CCSD(T) at $P_{\mathrm{CCSD(T)}}=252$ GPa and $V_{\mathrm{CCSD(T)}}=5.5$ $\mathrm{cm}^3/\mathrm{mol}$]. This is due to a fortuitous error cancellation for neon between the two-body and three-body contributions to the total pressure as shown in Fig. 6. At $V=3$ $\mathrm{cm}^3/\mathrm{mol}$ the MP2 two-body term overestimates the pressure by 5.8 GPa compared to the CCSD(T) result but underestimates it by 6.8 GPa in the three-body term. These cancellation effects (different signs of $\Delta P = P_{\mathrm{CCSD(T)}} - P_{\mathrm{MP}n}$) for the two-body compared to the three-body term are seen at all levels of theory.

As pointed out above, for neon both the repulsive region in the two-body term and the attractive region in the three-body term are entered at too large interatomic distances, leading to overestimated pressures in the two-body and underestimated pressures in the three-body term. At small volumes, the interplay of these effects leads to the nonmonotonous behavior of ΔP as seen in Fig. 5. Such cancellation effects do not occur for argon, where, for example, attractive interactions are underestimated in the two-body term at the MP2 level of theory, and the onset of the repulsive region appears at a smaller internuclear distance compared to

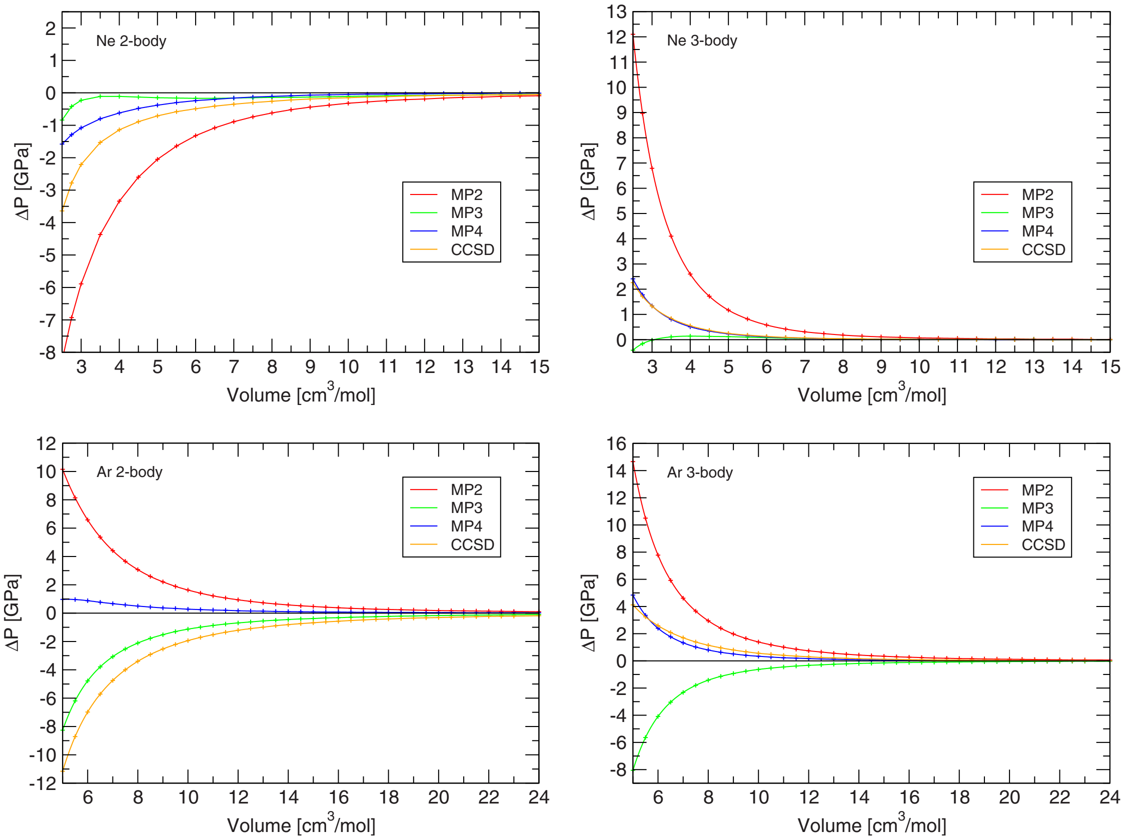

FIG. 6. (Color online) Deviation of the calculated *n*-body contribution to the pressure from our CCSD(T) result, i.e., $\Delta P = P_{\mathrm{CCSD(T)}} - P_M$, where M stands for MP2, MP3, MP4, and CCSD.

CCSD(T). Thus, errors in the two-body and three-body contribution to the total pressure are of the same sign; this holds for all MP*n* levels of theory for argon.

IV. CONCLUSIONS

We demonstrated that within the Møller-Plesset perturbation series describing electron correlation, only MP4 gives results for solid neon and argon in good agreement with experiment. Deviations from experimental values can be traced back mainly to deficiencies in the two-body term, and at the MP2 level of theory in the underestimation of the repulsive Axilrod-Teller-Muto three-body term. At the CCSD(T) level of theory the lattice constants, cohesive energies and bulk moduli are in good agreement with experiment. Further improvements require a better two-body term, for example, by including relativistic effects and going beyond the CCSD(T) level of theory (see Refs. 67 and 68), a full three-dimensional fit for the three-body term (see, for example, Refs. 102 and 103), and consideration of the four-body term. Moreover, we showed that the MP*n* convergence deteriorates at very high pressures as one expects. Thus, the application of second-order Møller-Plesset theory to study insulators, especially under very high pressure, has to be taken with some care.

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[1] A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor, J. Chem. Phys. **115**, 2389 (2001).
[2] A. Landau, E. Eliav, Y. Ishikawa, and U. Kaldor, J. Chem. Phys. **121**, 6634 (2004).
[3] E. Eliav, S. Shmulyian, U. Kaldor, and Y. Ishikawa, J. Chem. Phys. **109**, 3954 (1998).
[4] E. Eliav, A. Landau, Y. Ishikawa, and U. Kaldor, J. Phys. B **35**, 1693 (2002).
[5] T. Helgaker, W. Klopper, and D. P. Tew, Mol. Phys. **106**, 2107 (2008).
[6] W. Klopper, B. Ruscic, D. P. Tew, F. A. Bischoff, and S. Wolf-

segger, Chem. Phys. **356**, 14 (2009).
[7] Y. J. Bomble, J. Vázquez, M. Kállay, C. Michauk, P. G. Szalay, A. G. Császár, J. Gauss, and J. F. Stanton, J. Chem. Phys. **125**, 064108 (2006).
[8] S. Kurth, J. P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).
[9] Chr. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[10] C. Pisani, M. Busso, G. Capecchi, S. Casassa, R. Dovesi, L. Maschio, C. Zicovich-Wilson, and M. Schütz, J. Chem. Phys. **122**, 094113 (2005).
[11] C. Pisani, L. Maschio, S. Casassa, M. Halo, M. Schütz, and D. Usvyat, J. Comput. Chem. **29**, 2113 (2008).
[12] J. Harl and G. Kresse, Phys. Rev. B **77**, 045136 (2008).
[13] J. Harl and G. Kresse, Phys. Rev. Lett. **103**, 056401 (2009).
[14] B. G. Janesko, T. M. Henderson, and G. E. Scuseria, J. Chem. Phys. **130**, 081105 (2009).
[15] H. Stoll, Phys. Rev. B **46**, 6700 (1992).
[16] H. Stoll, Chem. Phys. Lett. **191**, 548 (1992).
[17] B. Paulus, Phys. Rep. **428**, 1 (2006).
[18] H. Stoll, Mol. Phys. **108**, 243 (2010).
[19] B. Paulus, K. Rościszewski, N. Gaston, P. Schwerdtfeger, and H. Stoll, Phys. Rev. B **70**, 165106 (2004).
[20] H. Stoll, B. Paulus, and P. Fulde, J. Chem. Phys. **123**, 144108 (2005).
[21] E. Voloshina, B. Paulus, and H. Stoll, J. Phys.: Conf. Ser. **117**, 012029 (2008).
[22] A. Hermann and P. Schwerdtfeger, Phys. Rev. Lett. **101**, 183005 (2008).
[23] H. Stoll, B. Paulus, and P. Fulde, Chem. Phys. Lett. **469**, 90 (2009).
[24] H. Stoll, J. Phys. Chem. A **113**, 11483 (2009).
[25] T. Shiozaki and S. Hirata, J. Chem. Phys. **132**, 151101 (2010).
[26] *Molecular Interactions: From van der Waals to Strongly Bound Complexes*, edited by S. Scheiner (Wiley, New York, 1994).
[27] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).
[28] Y. Muto, Proc. Phys. Math. Soc. Jpn. **17**, 629 (1943).
[29] A. Hermann and P. Schwerdtfeger, J. Chem. Phys. **131**, 244508 (2009).
[30] G. Chałasiński, M. M. Szczęśniak, and R. A. Kendall, J. Chem. Phys. **101**, 8860 (1994).
[31] A. Kumar and A. J. Thakkar, J. Chem. Phys. **132**, 074301 (2010).
[32] A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. **21**, 657 (1971).
[33] E. Blaisten-Barojas, O. Novaro, and L. W. Bruch, Mol. Phys. **37**, 599 (1979).
[34] W. J. Meath and M. Koulis, J. Mol. Struct.: THEOCHEM **226**, 1 (1991).
[35] V. F. Lotrich and K. Szalewicz, Phys. Rev. Lett. **79**, 1301 (1997).
[36] G. Chałasiński and M. Gutowski, Chem. Rev. **88**, 943 (1988).
[37] G. Chałasiński and M. M. Szczesniak, Chem. Rev. **94**, 1723 (1994).
[38] G. Chałasiński and M. M. Szczęśniak, Chem. Rev. **100**, 4227 (2000).
[39] K. Rościszewski, B. Paulus, P. Fulde, and H. Stoll, Phys. Rev. B **60**, 7905 (1999).
[40] K. Rościszewski, B. Paulus, P. Fulde, and H. Stoll, Phys. Rev. B **62**, 5482 (2000).
[41] P. Schwerdtfeger, N. Gaston, R. P. Krawczyk, R. Tonner, and G. E. Moyano, Phys. Rev. B **73**, 064112 (2006).
[42] N. C. Handy, P. J. Knowles, and K. Somasundram, Theor. Chim. Acta **68**, 87 (1985).
[43] K. Raghavachari, J. A. Pople, E. S. Replogle, and M. Head-Gordon, J. Phys. Chem. **94**, 5579 (1990).
[44] P. Schwerdtfeger and J. Ischtwan, J. Mol. Struct. THEOCHEM **306**, 9 (1994).
[45] D. Cremer and Z. He, J. Phys. Chem. **100**, 6173 (1996).
[46] M. L. Leininger, W. D. Allen, H. F. Schaefer III, and C. D. Sherrill, J. Chem. Phys. **112**, 9213 (2000).
[47] F. Stillinger, J. Chem. Phys. **112**, 9711 (2000).
[48] B. Forsberg, Z. He, Y. He, and D. Cremer, Int. J. Quantum Chem. **76**, 306 (2000).
[49] D. Usvyat, L. Maschio, F. R. Manby, S. Casassa, M. Schütz, and C. Pisani, Phys. Rev. B **76**, 075102 (2007).
[50] P. Schwerdtfeger and A. Hermann, Phys. Rev. B **80**, 064106 (2009).
[51] P. Schwerdtfeger, Computer code SAMBA: a solid-state approach using a many-body ansatz, Massey University, Auckland, 2010.
[52] A. Hermann, R. P. Krawczyk, M. Lein, P. Schwerdtfeger, I. P. Hamilton, and J. J. P. Stewart, Phys. Rev. A **76**, 013202 (2007).
[53] H.-J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobhyn, F. Eckert, C. Hampel, G. Hetzer, A. W. Lloyd, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, and T. Thorsteinsson, MOLPRO, version 2006.1, a package of *ab initio* programs, see http://www.molpro.net. (2006). See http://www.molpro.net
[54] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[55] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).
[56] A. K. Wilson, T. Van Mourik, and T. H. Dunning, Jr., J. Mol. Struct.: THEOCHEM **388**, 339 (1996).
[57] T. Van Mourik and T. H. Dunning, Jr., Int. J. Quantum Chem. **76**, 205 (2000).
[58] A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen, and A. K. Wilson, Chem. Phys. Lett. **286**, 243 (1998).
[59] S. F. Boys and F. Bernardi, Mol. Phys. **19**, 553 (1970).
[60] J. E. Jones and A. E. Ingham, Proc. R. Soc. London, Ser. A **107**, 636 (1925).
[61] R. Jaquet, in *Potential Energy Surfaces*, edited by A. F. Sax (Springer, Berlin, 1999).
[62] L. W. Bruch and I. J. McGee, J. Chem. Phys. **59**, 409 (1973).
[63] P. Loubeyre, Phys. Rev. Lett. **58**, 1857 (1987).
[64] Yu. A. Freiman and S. M. Tretyak, Fiz. Nizk. Temp. **33**, 719 (2007).
[65] J. A. Barker, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic Press, London, 1967), p. 212.
[66] K. T. Tang and J. P. Toennies, J. Chem. Phys. **80**, 3726 (1984).
[67] R. Hellmann, E. Bich, and E. Vogel, Mol. Phys. **106**, 133 (2008).
[68] B. Jäger, R. Hellmann, E. Bich, and E. Vogel, Mol. Phys. **107**, 2181 (2009).
[69] J. W. Cooley, Math. Comput. **15**, 363 (1961).
[70] B. Numerov, Publ. Obs. Central Astrophys. Russ. **2**, 188 (1933).
[71] J. Kohanoff, *Electronic Structure Calculations for Solids and Molecules: Theory and Computational Methods* (Cambridge University Press, Cambridge, England, 2006).
[72] G. E. Moyano, P. Schwerdtfeger, and K. Rościszewski, Phys.

Rev. B **75**, 024101 (2007).

[73] A. Wüest and F. Merkt, J. Chem. Phys. **118**, 8807 (2003).

[74] J. F. Ogilvie and F. Y. H. Wang, J. Mol. Struct. **273**, 277 (1992).

[75] P. R. Herman, P. E. LaRoque, and B. P. Stoicheff, J. Chem. Phys. **89**, 4535 (1988).

[76] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Constants of Diatomic Molecules Vol. IV (Van Nostrand, New York, 1979).

[77] G. Chałasiński, D. J. Funk, J. Simons, and W. H. Breckenridge, J. Chem. Phys. **87**, 3569 (1987).

[78] R. J. Bell and I. J. Zucker, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic Press, London, 1967), p. 122.

[79] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry* (McGraw-Hill, New York, 1989).

[80] G. Chałasiński and M. M. Szcześniak, Mol. Phys. **63**, 205 (1988).

[81] G. Chałasiński, M. M. Szczęśniak, and S. M. Cybulski, J. Chem. Phys. **92**, 2481 (1990).

[82] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. **150**, 703 (1966).

[83] D. N. Batchelder, D. L. Losee, and R. O. Simmons, Phys. Rev. **162**, 767 (1967).

[84] D. N. Batchelder, D. L. Losee, and R. O. Simmons, Phys. Rev. **173**, 873 (1968).

[85] G. J. McConville, J. Chem. Phys. **60**, 4093 (1974).

[86] Y. Endoh, G. Shirane, and J. Skalyo, Jr., Phys. Rev. B **11**, 1681 (1975).

[87] L. A. Schwalbe, R. K. Crawford, H. H. Chen, and R. A. Aziz, J. Chem. Phys. **66**, 4493 (1977).

[88] Y. Fei, A. Ricolleau, M. Frank, K. Mibe, G. Shen, and V. Prakapenka, Proc. Natl. Acad. Sci. U.S.A. **104**, 9182 (2007).

[89] E. L. Pollock, T. A. Bruce, G. V. Chester, and J. A. Krumhansl, Phys. Rev. B **5**, 4180 (1972).

[90] L. W. Finger, R. M. Hazen, G. Zou, H. K. Mao, and P. M. Bell, Appl. Phys. Lett. **39**, 892 (1981).

[91] M. Grimsditch, P. Loubeyre, and A. Polian, Phys. Rev. B **33**, 7192 (1986).

[92] R. J. Hemley, C. S. Zha, A. P. Jephcoat, H. K. Mao, L. W. Finger, and D. E. Cox, Phys. Rev. B **39**, 11820 (1989).

[93] A. Dewaele, F. Datchi, P. Loubeyre, and M. Mezouar, Phys. Rev. B **77**, 094106 (2008).

[94] H. Shimizu, H. Imaeda, T. Kume, and S. Sasaki, Phys. Rev. B **71**, 014108 (2005).

[95] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.), Circ. No. 467 (U.S. GPO, Washington, DC, 1958).

[96] S. A. Khairallah and B. Militzer, Phys. Rev. Lett. **101**, 106407 (2008).

[97] P. M. Celliers, P. Loubeyre, J. H. Eggert, S. Brygoo, R. S. McWilliams, D. G. Hicks, T. R. Boehly, R. Jeanloz, and G. W. Collins, Phys. Rev. Lett. **104**, 184503 (2010).

[98] R. Reichlin, K. E. Brister, A. K. McMahan, M. Ross, S. Martin, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. Lett. **62**, 669 (1989).

[99] E. E. Koch, V. Saile, N. Schwentner, and M. Skibowski, Chem. Phys. Lett. **28**, 562 (1974).

[100] D. Pudewill, F.-J. Himpsel, V. Saile, N. Schwentner, M. Skibowski, and E. E. Koch, Phys. Status Solidi B **74**, 485 (1976).

[101] N. Schwentner, F.-J. Himpsel, V. Saile, M. Skibowski, W. Steinmann, and E. E. Koch, Phys. Rev. Lett. **34**, 528 (1975).

[102] V. F. Lotrich and K. Szalewicz, J. Chem. Phys. **106**, 9688 (1997).

[103] V. F. Lotrich and K. Szalewicz, J. Chem. Phys. **112**, 112 (2000).