Complete basis set limit second-order Møller–Plesset calculations for the fcc lattices of neon, argon, krypton, and xenon

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Complete basis set (CBS) limit calculations using second-order Møller–Plesset (MP2) theory for electron correlation within a many-body expansion of the interaction potential up to third order are carried out for the fcc lattices of Ne, Ar, Kr, and Xe. Lattice constants and cohesive energies from recent localized MP2 solid-state calculations by Halo *et al.* [Chem. Phys. Lett. **467**, 294 (2009)] are in reasonable agreement with our CBS limit results. A detailed analysis reveals that MP2 severely underestimates long-range three-body effects, thus the Axilrod–Teller term is incorrectly described causing bond contractions for all rare gas solids considered. Further, any deviations in the MP2 lattice constant, cohesive energy, and bulk modulus can be traced back to inaccuracies in the binding energy and equilibrium distance of the rare gas dimer. Without inclusion of phonon dispersion, MP2 prefers the hcp over the fcc crystal structure for all rare gas solids considered. © *2009 American Institute of Physics*. [doi:10.1063/1.3279303]

I. INTRODUCTION

The quantum theoretical treatment of solids is currently dominated by density functional theory (DFT), which is in principle exact and avoids the construction of the complicated many-electron wave function.[1–3] However, the many shortfalls of the numerous approximations used for the exchange-correlation functional are well known and documented,[4–10] and these cannot be very easily fixed.[11,12] For example, the incorrect long-range behavior of the one-particle density originating from the various approximations used for the formally exact exchange-correlation functional results in an erratic behavior for dispersive type of interactions,[13] leading to inaccurate results for the interaction of closed shell atoms such as group 2 and 12 metals,[14] or rare gas solids.[15,16] Recent improvements to fix the long-range part of the one-particle density include new exchange-correlation functionals,[9,17] the addition of Van der Waals type interaction terms,[18–24] exact Hartree–Fock exchange plus electron correlation in the long-range,[25–29] the use of the random-phase approximation[30] introduced into DFT,[30–34] and recently further developed by Kresse and co-workers,[35–37] symmetry-adapted perturbation theory on top of DFT,[38–40] self-consistent polarization DFT,[41] tailored correlation functionals on top of Hartree–Fock,[42,43] nonlocal effective potentials to simulate dispersion forces,[44] and many more. Some of these approximations are in fact using wave function based post-Hartree–Fock methods to account for a better description of electron correlation, and should therefore not be considered as pure DFT anymore. Despite the improvement in nonempirical generalized gradient approximations to account for dispersive type of interactions,[6,15] it is currently not clear how some of these methods perform in general for weakly interacting systems. For example, describing cor-

rectly the energetic sequence of the different polymorphs for molecular crystals is a difficult task and remains a challenge for solid-state theory.[45,46]

Wave function based methods also exhibit a number of difficulties in correctly describing the solid state.[47] Apart from the computational demand of accurate post-Hartree–Fock methods such as coupled cluster theory,[48,49] it is unclear how electron correlation can accurately be accounted for if the electronic band gap closes.[50] Recent important developments into this direction were the implementation of local second-order Møller–Plesset (LMP2) theory into the program system CRYSTAL,[51] and the incremental method developed by Stoll.[52–54] Stoll's method of increments has recently been applied successfully to calculate the solid-state structures for a variety of electronic systems including metals.[55–60] If coupled-cluster theory is used to obtain correlation energies, the incremental method is very accurate but computationally quite demanding and cumbersome, although an efficient algorithm for this method has recently been developed by Friedrich and Dolg.[61] The computationally much less demanding LMP2 method diverges for metallic systems, since single-particle band gaps appear in the denominator of the perturbation series. It is thus applicable only to medium or large band-gap materials, i.e., insulators. Furthermore, Hartree–Fock calculations using Gaussian type basis sets often face difficulties regarding the self-consistent field (SCF) convergence if diffuse basis functions are used, which are necessary for the correct description of weakly interacting systems. Such calculations are also plagued by sizable basis set superposition errors which cannot be neglected in the treatment of dispersive type of interactions. Hence, it is often difficult to estimate the errors coming from the LMP2 approximation or from the finite basis set applied. For this reason we decided to carry out complete basis set (CBS) limit calculations at the MP2 level of theory within a many-body

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expansion of the interaction potential up to third order for the solid-state structures of the rare gas elements Ne, Ar, Kr, and Xe. This allows to assess the accuracy of recent LMP2 type calculations by Halo et al.[62–64] and serves as a benchmark for future implementations of the LMP2 method. Also, a comparison of CBS limit MP2 results to experimental data gives a more accurate and complete insight into the performance of this method for solid state calculations. For example, Hobza and co-workers[65] pointed out that dispersive interactions are overestimated by MP2, and this has been addressed recently in more detail for the rare gas dimers by Tkatchenko et al.[66] In fact, MP3 underestimates dispersion interactions almost as much as MP2 overestimates them. In order to improve this situation, very recently Marchetti and Werner[67] introduced the dispersion-weighted MP2 (DW-MP2) approximation as a variant of Grimme's spin-component-scaled MP2 (SCS-MP2).[68] Another interesting aspect is the recent claim that LMP2 prefers the fcc structure over the hcp structure for argon by about 22 cm^{-1} (Ref. [62]) in agreement with experiment, but contrary to previous coupled cluster and many-body expansion results.[16,69]

II. COMPUTATIONAL DETAILS

For the solid-state calculations we used a truncated expansion of the many-body interaction potential using translational symmetry for the rare gas solids Ne, Ar, Kr, and Xe to obtain the cohesive energy E_{coh} dependent on the volume V of the fcc crystal,[16]

$$E_{coh}(N,V) = \sum_n E^{(n)}(N,V)$$
$$= \frac{1}{2}\sum_i^N E^{(2)}(r_{0i}) + \frac{1}{3}\sum_{i<j}^N E^{(3)}(r_{0i},r_{0j},r_{ij}) + \cdots, \quad (1)$$

where r_{0i} is the distance between the innermost (central atom) and atom i in the fcc lattice for a specific lattice constant a and corresponding volume $V=a^3/4$. The cluster size N for the fcc lattice was chosen sufficiently large to achieve convergence of the optimized lattice constant to four digits behind the decimal point.[16] The many-body expansion is in principle exact, but computationally feasible only if the series expansion (1) converges fast, which is the case for the rare-gas solids at low pressures.[16,70,71] The lattice dynamics was included within the harmonic approximation, that is zero-point vibrational energy contributions (E_0) were included using the Einstein approximation[3] by moving one atom in the static field of all other atoms. This gives the simple expression

$$E_0(V) = 3\hbar\omega_E(V)/2, \quad (2)$$

where ω_E is the Einstein frequency obtained from two-body forces only at a specific volume of the crystal.[16] The program system SAMBA was used for all solid-state calculations.[72]

The dimer interaction energies $E^{(2)}(r)$ were calculated for a range of atomic distances r between 4.25 and 11.33 a.u. for Ne, and between 5.66 and 15.11 a.u. for the other elements. The same sets of distances r were used as side lengths

of equilateral triangles to calculate trimer interaction energies $E^{(3)}(r_{12},r_{13},r_{23})$ with $r=r_{12}=r_{13}=r_{23}$. The calculations were performed using the quantum chemistry packages GAUSSIAN03 (Ref. [73]) and MOLPRO (2006 version).[74] All MP2 calculations utilize the frozen-core approximation keeping only the occupied valence n sp-space active. Interaction energies are corrected for basis set superposition errors using the Boys–Bernardi approach,[75]

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

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

Here $E_X^{(2)}$ and $E_X^{(3)}$ denote the dimer and trimer interaction energies for the rare gas element X, and G denotes the presence of ghost atom basis set(s) at the position(s) otherwise occupied by an atom X. The dimer interaction energy is then fitted in a least-squares procedure to an extended Lennard-Jones potential,[16]

$$E_X^{(2)}(r) = \sum_{n=1}^{6} \frac{C_{2n+4}}{r^{2n+4}}, \quad (5)$$

and the trimer interaction potential is fitted to an extended Axilrod–Teller potential that accounts for short range attraction as well as long-range dispersive repulsion interactions,[71]

$$E_X^{(3)}(r_{ij},r_{jk},r_{ik}) = f_\theta \left(\frac{C_{AT}}{r_g^9} + e^{-\alpha r_s} \sum_{n=0}^{3} A_{2n} r_g^{2n} \right), \quad (6)$$

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

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

This potential, when derived from coupled-cluster calculations, led recently to very accurate results for the equation-of-state for solid neon.[71] For Ne and Ar, all-electron augmented correlation consistent basis sets aug-cc-pV5Z and aug-cc-pV6Z[76–79] were used to obtain $E^{(2)}$ and $E^{(3)}$. For Kr and Xe, the small-core pseudopotential augmented correlation consistent basis sets aug-cc-pVQZ-PP and aug-cc-pV5Z-PP (Ref. [80]) were used. For all elements, an extrapolation of the correlation energy to the CBS limit was performed using the ansatz by Halkier et al.,[81]

$$E_{MP2}^c(x) = E_{MP2}^c(CBS) + \beta x^{-3}, \quad (7)$$

where x is the cardinal number of the aug-cc-pVxZ(-PP) basis set. For $x=5$ the Hartree–Fock limit is already reached within the set accuracy, and the SCF energies are therefore not extrapolated, but taken from the aug-cc-pV6Z (aug-cc-pV5Z-PP) calculations for Ne and Ar (Kr and Xe), respectively. The adjusted coefficients from the potential energy fits are listed in Table I. The spectroscopic constants were obtained numerically using the Numerov–Cooley procedure.[82,83]

III. RESULTS AND DISCUSSION

The calculated spectroscopic constants for the rare gas dimers are listed in Table II together with other MP2, coupled cluster, and long-range corrected DFT results and

TABLE I. Coefficients for the X_2 and X_3 (X=Ne, Ar, Kr, Xe) potential energy hypersurfaces as defined in Eqs. (5) and (6) (in atomic units).

Coeff.	Ne	Ar	Kr	Xe
		Two-body		
C_6	$-8.911\ 90\times10^0$	$-1.336\ 54\times10^2$	$-2.435\ 69\times10^2$	$-6.836\ 65\times10^2$
C_8	$8.513\ 97\times10^2$	$2.074\ 23\times10^4$	$4.115\ 01\times10^4$	$1.696\ 08\times10^5$
C_{10}	$-8.562\ 74\times10^4$	$-3.128\ 97\times10^6$	$-7.964\ 56\times10^6$	$-3.614\ 86\times10^7$
C_{12}	$3.326\ 90\times10^6$	$1.818\ 17\times10^8$	$5.533\ 10\times10^8$	$2.958\ 28\times10^9$
C_{14}	$-4.673\ 58\times10^7$	$-4.099\ 80\times10^9$	$-1.457\ 18\times10^{10}$	$-9.666\ 61\times10^{10}$
C_{16}	$2.323\ 08\times10^8$	$3.332\ 36\times10^{10}$	$1.363\ 94\times10^{11}$	$1.147\ 08\times10^{12}$
		Three-body		
A_0	$6.947\ 52\times10^1$	$1.667\ 05\times10^2$	$6.935\ 09\times10^2$	$3.042\ 10\times10^3$
A_2	$-8.643\ 89\times10^1$	$-9.592\ 91\times10^1$	$-1.403\ 95\times10^2$	$-2.943\ 41\times10^2$
A_4	$1.985\ 56\times10^0$	$2.514\ 17\times10^0$	$3.098\ 03\times10^0$	$4.927\ 79\times10^0$
A_6	$-6.285\ 15\times10^{-4}$	$-1.351\ 33\times10^{-2}$	$-1.447\ 81\times10^{-2}$	$-1.891\ 66\times10^{-2}$
α	$1.205\ 70\times10^0$	$8.817\ 84\times10^{-1}$	$8.159\ 44\times10^{-1}$	$7.492\ 99\times10^{-1}$
C_{AT}	$7.024\ 70\times10^{-2}$	$1.158\ 94\times10^{-2}$	$1.536\ 60\times10^{-2}$	$6.048\ 72\times10^1$

experimental data. The corresponding MP2 potential curves are shown in Fig. 1. The calculated MP2 bond distances for the rare gas dimers Ar$_2$, Kr$_2$, and Xe$_2$ are about 0.1 Å below the very precise CCSDTQ results reported recently by Jäger et al.,[85] or the CCSD(T) results by Goll et al.,[25] Woon,[89] or van Mourik,[90] and below the experimental bond distances.[86,87] The neon dimer is an exception here with the MP2 distance being about 0.1 Å above the experimental value or the precise CCSDTQ result of Hellman et al.[84] Our MP2 CBS limit results are in reasonable agreement with results reported earlier by Halo et al.,[64] but deviate in the case of Ne$_2$ due to basis set deficiencies in their calculations. We note that the CBS MP2 results for neon are in less good

agreement with experiment than for example the long-range corrected DFT results published by Hirao and co-workers.[21] The MP2 method is well known to overbind, thus leading to too short bond distances, and resulting in an overestimation of binding energies. This is indeed the case for the rare gas dimers except for Ne$_2$, where the interaction is rather weak. It was noted before that MP2 tends to overestimate dispersive type of interactions.[65,91] We will see below how these errors for the diatomics propagate into the rare gas solids.

Figure 2 shows the three-body MP2 curves $E^{(3)}(r)$ for the equilateral triangle (D_{3h} symmetry) for all rare gas elements. $E_{Ne}^{(3)}(r)$ is extremely small around the equilibrium dis-

TABLE II. Spectroscopic constants r_e (in angstrom), D_e, ω_e, and $\omega_e x_e$ (in cm^{-1}) for the diatomics X_2 (X=Ne, Ar, Kr, Xe) compared to experiment and to results from other authors, and potential maximum positions r_m (in angstrom) and values $E^{(3)}(r_m)$ (in 10^{-6} a.u.) for the D_{3h} path of the three-body potential.

| Prop.	Method	Reference	Ne	Ar	Kr	Xe
		Two-body				
r_e	MP2		3.198	3.725	3.978	4.347
	MP2	64	3.10	3.75	4.05	4.40
	CCSD(T)	25, 84, and 85	3.090	3.762	4.076	4.471
	LC-DFT	21	3.077	3.890	⋯	⋯
	B3LYP+vdW	19	3.000	3.897	⋯	⋯
	Exp.	86–88	3.094	3.756	4.008	4.363
D_e	MP2		18.9	114.6	164.9	231.0
	MP2	64	22.5	100.1	139.3	193.8
	CCSD(T)	25, 84, and 85	29.3	99.47	120.8	161.2
	LC-DFT	21	29	84	⋯	⋯
	B3LYP+vdW	19	15	31	⋯	⋯
	Exp.	86–88	29.4	99.5	139.8	196.2
ω_e	MP2		22.5	33.7	26.7	23.4
	CCSD(T)	25	25.8	27.9	21.8	18.5
	Exp.	86–88	21.3	31.4	23.8	21.1
$\omega_e x_e$	MP2		6.9	3.0	1.4	0.8
	Exp.	86 and 87	7.6	2.9	1.3	0.7
		Three-body				
r_m	MP2		3.624	3.977	4.190	4.646
$E^{(3)}(r_m)$	MP2		0.0106	1.067	2.634	3.846
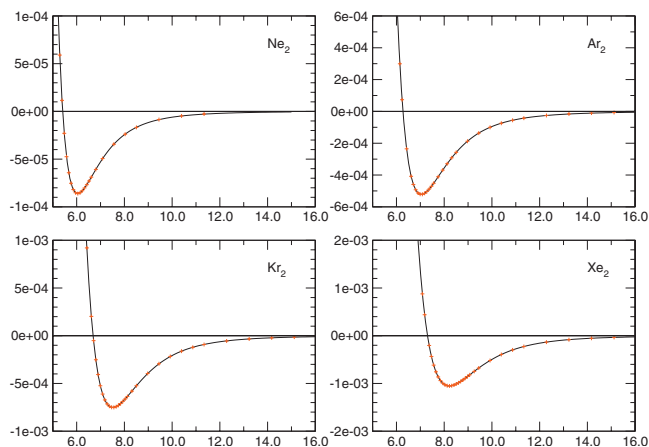
FIG. 1. X_2 (X=Ne, Ar, Kr, Xe) potential energy curves. The red plus signs indicate CBS limit data points and the black solid line indicates fit with ELJ potential from Eq. (5), parameters from Table I. All energies and distances are in atomic units.

tance, which required tighter convergence criteria for the SCF procedure in order to avoid numerical errors. In fact, $E_{Ne}^{(3)}$ is about two orders of magnitude smaller in the long-range part than the corresponding CCSD(T) values published recently.[71] This implies that double excitations cannot describe three-body dispersive type of interactions, which comes at no surprise. As a consequence, the MP2 Axilrod–Teller coefficient (C_{AT}=0.07 a.u., see Table I) for Ne is not even close to the experimentally derived value of 12.0 a.u. (Ref. 92). In fact, all the MP2 Axilrod–Teller coefficients are orders of magnitude smaller than the literature values of 518 a.u. for Ar_3, 1554 a.u. for Kr_3, and 5605 a.u. for Xe_3.[92] Moreover, the equilibrium bond distances for the rare gas dimers are much smaller than the potential maximum position r_m listed in Table I, and well within the attractive region of the MP2 three-body potential. Hence, the combination of the severe underestimation of the repulsive region in the three-body potential and the fact that $r_e < r_m$ will lead to a contraction in the rare-gas crystals and an increased cohesive
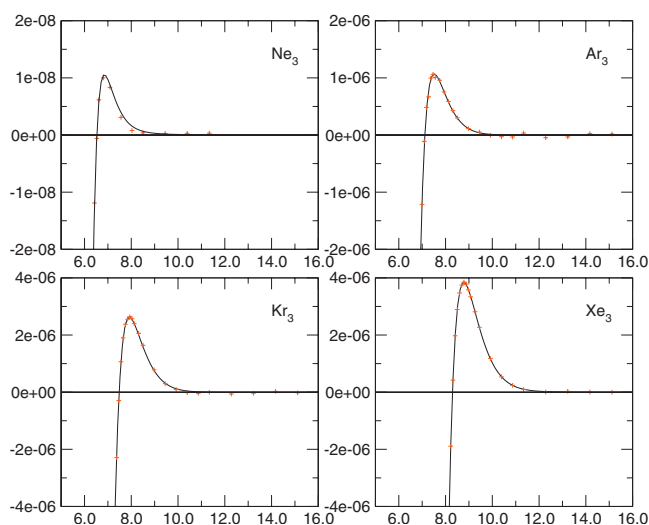

FIG. 2. X_3 (X=Ne, Ar, Kr, Xe) three-body curves for the equilateral triangle. Red plus signs indicate CBS limit data points and black solid lines indicate fits with potential from Eq. (6), parameters from Table I. All energies and distances are in atomic units.

energy when three-body terms are included in the solid-state calculations. This is in stark contrast with what is found at the coupled-cluster level of theory.[69,71] As another consequence, the many-body expansion for the MP2 interaction potential converges much faster in the long-range than the exact decomposition, and we expect that four-body forces can be neglected in the long range.

The solid-state results are collected in Table III in comparison with experiment and results from other authors. As expected the MP2 lattice constants are smaller than the coupled-cluster [CCSD(T)] values of Stoll and co-workers[69,102] except for neon, which reflects the wrong behavior of the MP2 two-body interaction. For all solids the three-body effect is attractive at the solid-state nearest-neighbor distance, and therefore opposite in sign compared to more accurate coupled-cluster results.[69,71] For example, for Xe_2 the MP2 three-body contribution to the cohesive energy is attractive with −38 cm⁻¹ compared to the repulsive contribution of +32 cm⁻¹ at the coupled cluster level.[69] Our lattice constants (not corrected for zero-point vibrational energy) are, except for neon, smaller than the MP2 values of Halo *et al.*,[64] and the deviations in the cohesive energies are as much as 9% for neon and not much smaller for the other rare gas solids. The bulk modulus is extremely sensitive to the lattice constants and here we have larger deviations from the LMP2 values.

In order to compare to experimental data one must include the zero-point vibrational energy. This is done here using the Einstein approximation. The MP2 ($E^{(2)}+E^{(3)}+E_0$) lattice constants for neon is too large compared with experiment, while for the heavier rare gas elements we obtain lattice constants which are too small. For the cohesive energies we obtain much larger deviations. For Ne the MP2 cohesive energy is underestimated by 37%, and for Ar, Kr, and Xe overestimated by 29%, 31%, and 33%, respectively. Similar large deviations are observed for the bulk moduli.

It may be useful here to discuss some approximate relations between the properties of the rare gas dimers and the respective solid state properties. If we compare the nearest neighbor distances r_{NN} in the crystal obtained from the lattice constants a ($r_{NN}=a/\sqrt{2}$) with the MP2 equilibrium distances r_e of the dimers, we obtain from a simple Lennard-Jones ansatz for the solid state interaction potential,

$$r_{NN} = \left(\frac{L_{12}}{L_6}\right)^{1/6} r_e, \qquad (8)$$

where L_6 and L_{12} belong to a set of Lennard–Jones–Ingham coefficients for the fcc lattice,[103] which have been derived recently to high precision.[16] This gives $r_e/r_{NN}=1.0296$, which is the additional attractive two-body interactions in the rare-gas crystal lead to a contraction compared to the rare gas dimer. From our MP2 calculations we obtain $r_e/r_{NN}=1.018$ for Ne, 1.022 for Ar and Kr, and 1.023 for Xe considering two-body forces only. Hence this simple relation is quite well fulfilled at the MP2 level of theory, and consequently any deviation we obtain for the crystal lattice constants can be traced back to errors in the bond distance r_e for the dimer. In a similar way we have for the Lennard-Jones cohesive energy[16]

TABLE III. Calculated MP2 lattice parameters a (angstrom), cohesive energies E_{coh} (cm^{-1}) and bulk moduli B (kbar) for the rare gas solids Ne, Ar, Kr, and Xe in comparison with experiment and results from other authors.

Prop.	Method	Reference	Ne	Ar	Kr	Xe
a	MP2 $E^{(2)}$		4.430	5.153	5.502	6.012
	MP2 $E^{(2)}+E^{(3)}$		4.423	5.134	5.481	5.974
	LMP2	64	4.35	5.20	5.50	6.10
	CCSD(T)	69	4.297	5.251	5.598	6.087
	MP2 $E^{(2)}+E^{(3)}+E_0$		4.660	5.192	5.514	5.996
	CCSD(T)$+E_0$	69	4.468	5.311	5.633	6.111
	Exp.	93–96	4.464	5.300	5.646	6.132
E_{coh}	MP2 $E^{(2)}$		150.9	908.4	1292	1814
	MP2 $E^{(2)}+E^{(3)}$		151.5	912.6	1294	1827
	LMP2	64	165.5	852.7	1234	1693
	CCSD(T)	69	211.5	709.1	983.0	1372
	MP2 $E^{(2)}+E^{(3)}+E_0$		104.7	830.7	1230	1771
	CCSD(T)$+E_0$	69	164.8	645.9	935.8	1328
	Exp.	97 and 98	161.6	645.5	931.9	1319
B	MP2 $E^{(2)}$		12.4	44.0	50.6	53.7
	MP2 $E^{(2)}+E^{(3)}$		12.3	42.7	48.4	50.7
	LMP2	64	6.1	27.8	32.5	40.9
	CCSD(T)	69	18.8	33.1	36.1	39.6
	MP2 $E^{(2)}+E^{(3)}+E_0$		5.4	36.7	44.6	48.0
	CCSD(T)$+E_0$	69	10.4	27.9	32.9	37.2
	Exp.	94 and 99–101	11.0	26.7	36.1	36.4

$$E_{coh} = \frac{1}{2}\frac{L_6^2}{L_{12}}D_e, \qquad (9)$$

which gives $E_{coh}/D_e=8.6093$ for the fcc lattice. From our MP2 calculations we obtain $E_{coh}/D_e=7.98$ for Ne, 7.93 for Ar, 7.84 for Kr, and 7.85 for Xe considering two-body forces only. Again, this simple relation is reasonably well fulfilled and in agreement with the ratios obtained from more accurate potential curves,[16] and therefore errors in the cohesive energy can be traced back to errors in the dimer binding energy. For the bulk modulus we have[16]

$$B = L_{12}\left(\frac{2L_6}{L_{12}}\right)^{5/2}\frac{D_e}{r_e^3}. \qquad (10)$$

Hence the bulk modulus becomes sensitive to errors in both the binding energy and equilibrium bond distance of the dimer which is clearly seen in our results.

Finally we address the problem of the hcp/fcc lattice difference in energy. The question here is if MP2 correctly describes energy differences between polymorphic crystals. In a recent paper by Casassa et al.[62] it was stated that LMP2 favors fcc over hcp by 21.9 cm^{-1} for argon, which is in agreement with experiment where only the fcc phase is known. This, however, is in contradiction with previous coupled-cluster results by Stoll and co-workers[52,55] using an incremental method, and to results from many-body expansions carried out in our group.[16] There it was concluded that quantum fluctuations from the zero-point vibrational energy are responsible for the change from hcp to fcc and not the three-body force as originally claimed by Lotrich and Szalewicz.[104] The result by Casassa et al. is rather peculiar as the three-body forces are underestimated in the MP2 proce-

dure, and the question arises whether their result is related to differences in the localization procedure for the different crystal structures considered. We therefore optimized the hcp lattices at the MP2 level of theory taking both the two- and three-body forces into account and applying extremely tight convergence criteria as the energy differences between both lattice types are rather small. For all elements the MP2 CBS limit results show that the hcp lattice is preferred if zero-point vibration is neglected, in agreement with previous calculations.[16,52,55] The calculated energy difference between fcc and hcp $(E^{(2)}+E^{(3)})$ are 0.010 cm^{-1} for Ne, 0.113 cm^{-1} for Ar, 0.153 cm^{-1} for Kr, and 0.230 cm^{-1} for Xe. Hence, for the accurate determination of rare gas solids, and in general for polymorphs in molecular crystals, where rather small energy differences become relevant for the correct structure determination, one has to take great care of the approximation applied.

IV. CONCLUSIONS

We demonstrated the failure of MP2 to correctly describe long-range three-body dispersive type of interactions, which could be remedied by applying higher-order perturbation theory such as MP4 or by coupled-cluster theory. This error leads to an unphysical contraction of the fcc lattice. Besides this error in the three-body force, MP2 in general leads to lattice constants, cohesive energies, and bulk moduli for the rare gases which are not in good agreement with more accurate coupled-cluster results or experimental data. These deviations can be traced back to the incorrect description of rare gas dimers, which is the incorrect behavior of the MP2 two-body potential. The result that argon prefers crystallization in the fcc structure over hcp because of quantum fluc-

tuations remains unchallenged, and the use of LMP2 to describe small energy differences between polymorphs needs to be further explored.

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