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Ab initio calculation of ground-state properties of rare-gas crystals

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Cohesive energies, lattice constants, and bulk moduli have been calculated for the rare-gas crystals Ne through Xe. The results are based on a many-body expansion of the interaction energy, with two- and three-atom contributions evaluated in valence-only coupled-cluster calculations using relativistic pseudopotentials. Although the two-body contributions dominate the cohesive energy in all cases, the influence of three-body contributions is non-negligible and reaches nearly 7% of the cohesive energy for Xe.
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I. INTRODUCTION

The *ab initio* description of rare-gas crystals is a challenging problem of computational physics. Due to the weak van der Waals interaction, very accurate methods are necessary for calculating the ground-state properties of such crystals. A Hartree-Fock (HF) description does not yield binding at all; inclusion of electron correlation by means of perturbational methods such as second-order Møller-Plesset theory (MP2) usually leads to significant over-binding in the case of rare-gas dimers, and only with high-level correlated *ab initio* methods is it possible to reliably evaluate the van der Waals interaction. Density-functional methods, on the other hand, lead to severe overbinding for rare-gas dimers, in the local-density approximation (LDA);[1,2] with gradient-corrected functionals (GGA), results range from purely repulsive to weakly bonding,[1–4] but it is clear that the accuracy of quantum-chemical *ab initio* methods cannot be reached at this level.

Wave-function-based correlation methods have been mainly applied to dimers so far (see, e.g., Ref. 5 and references therein) and very rarely to crystals.[6] In the present paper, we want to apply an incremental method[7] to the rare-gas crystals neon, argon, krypton, and xenon, which was successfully applied to covalent[8] and ionic[9] crystals as well as to polymers[10] in the past. Here a many-body expansion of the ground-state energy is made in terms of rapidly convergent increments. Individual increments are determined in finite fragments of the solid and hence accessible via standard quantum-chemical *ab initio* calculations. A size-extensive correlation treatment is necessary for our purpose, and we use the coupled-cluster approach with single and double excitations and perturbative treatment of triples [CCSD(T)].

In Sec. II, we briefly sketch our method and describe some computational details. After discussing dimer results in Sec. III A, we proceed to the presentation and discussion of the results for the rare-gas crystals (Sec. III B). Conclusions follow in Sec. IV.

II. COMPUTATIONAL DETAILS

A. Method of increments

In our previous applications for ionic crystals and semiconductors, HF contributions to the ground-state energy of the crystal were taken from fully periodic calculations, and a many-body expansion in terms of local increments was made for electron-correlation contributions only. In the present case, where atomic interaction is mainly due to correlation effects and no long-range HF contributions are present, we expand the total ground-state energy as a whole:

$$E=\sum_{A}\epsilon(A)+\frac{1}{2!}\sum_{A,B}\Delta\epsilon(A,B)+\frac{1}{3!}\sum_{A,B,C}\Delta\epsilon(A,B,C)+\cdots. \tag{1}$$

Here A, B, and C denote (nonidentical) groups of occupied localized orbitals that are chosen as the s^2p^6 valence shells of the rare-gas atoms. The one-body terms $\epsilon(A)$ are simply free-atom energies. The two-body increments describe diatomic interactions and are calculated as

$$\Delta\epsilon(A,B)=\epsilon(A,B)-\epsilon(A)-\epsilon(B), \tag{2}$$

where $\epsilon(A,B)$ is the ground-state energy of the (isolated) composite system (A,B). The next terms $\Delta\epsilon(A,B,C)$ denote three-body contributions and are defined analogously as

$$\Delta\epsilon(A,B,C)=\epsilon(A,B,C)-\Delta\epsilon(A,B)-\Delta\epsilon(A,C)-\Delta\epsilon(B,C)-\epsilon(A)-\epsilon(B)-\epsilon(C). \tag{3}$$

Clearly, if the summation in Eq. (1) could be continued to infinity, the exact ground-state energy would be obtained. However, truncation is possible since the series rapidly converges with respect to the number of localized orbital groups treated simultaneously and also with respect to the spatial distance between these groups.

The individual increments $\epsilon(A)$, $\Delta\epsilon(A,B)$, and $\Delta\epsilon(A,B,C)$ are calculated at the CCSD(T) level correlating all valence electrons. Note that all energies needed for a

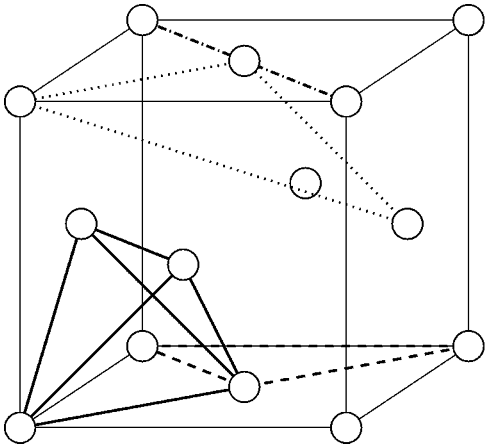

FIG. 1. Clusters used for the incremental expansion are shown in the fcc unit cell: Tetrahedron (solid line, one face defines the 60° three-atom cluster), 90° three-atom cluster (dashed line), 120° three-atom cluster (dotted line), and the linear three-atom cluster (dash-dotted line).

given increment are extracted from the same cluster of atoms, see Sec. II B. All calculations were performed using the *ab initio* program package MOLPRO96.[11]

B. Selection of the clusters

The low-temperature phase of rare-gas crystals is a dense-packed fcc structure with lattice constant *a* as shown in Fig. 1; the cluster fragments used for the calculation of the increments are depicted in the figure. For the two-body increments we considered three two-atom clusters, one with nearest-neighbor distance $(1/\sqrt{2})a$, one with next-nearest-neighbor distance *a*, and one with distance $\sqrt{\frac{3}{2}}a$ The weight factors per (primitive) unit cell are 6, 3, and 12, respectively. As three-atom clusters, we selected triangles two sides of which have nearest-neighbor distances. The possible angles are 60°, 90°, 120°, and 180°, with corresponding weight factors 8, 12, 24, and 6, respectively. For test calculations, we also considered a (regular) tetrahedron as a four-atom cluster with weight 2.

C. Pseudopotentials and basis sets

The heavier rare-gas crystals are only accessible to an *ab initio* treatment when the core shells are described by pseudopotentials. In our calculations, we used the energy-consistent pseudopotentials from Ref. 12, implicitly including scalar-relativistic effects. For Xe, we supplemented the pseudopotential by a core-polarization potential (CPP), in order to account for core-valence correlation effects; parameters were taken again from Ref. 12.

For a reliable description of the van der Waals interaction, a careful selection of the atomic basis sets is decisive. We started from the optimized $(6s6p3d1f)/[4s4p3d1f]$ (Ne: $(7s7p3d1f)/[4s4p3d1f]$) valence basis sets published with the pseudopotentials of Ref. 12 (basis A). In a first step, this basis was supplemented in an even-tempered way by diffuse $1s1p1d1f$ sets yielding basis *B*. (The ratio for the additional *f* exponent was chosen to be the same as for *d*.) Basis *C* is a $(8s8p6d6f)/[6s6p6d6f]$ (Ne: $(9s9p6d6f)/[6s6p6d6f]$) set, which was also published in Ref. 12 and which differs from *A* by adding two diffuse sp sets and introducing more flexible polarization sets. The most elaborate basis chosen for our calculations is a $(8s8p6d5f4g)/[7s7p6d5f4g]$ (Ne: $(9s9p6d5f4g)/[7s7p6d5f4g]$) basis set (basis D). We decontracted one sp set in basis *A* and added two diffuse sp functions in an even-tempered manner (scaling factor 2.81). The polarization sets were determined as follows: for Ne and Ar, we started with Dunnings $4d3f2g$ set[13] and supplemented it by diffuse $2d2f2g$ functions following the recipe given in Ref. 13; for Kr and Xe, we optimized an even-tempered $4d3f2g$ set at the CCSD energy of the free atom and added diffuse $2d2f2g$ functions in the same manner as above. The exponents of the polarization functions of basis *D* are listed in Table I.

TABLE I. Exponents (in a.u.) of the polarization functions of basis set *D*, see the text.

	Ne	Ar	Kr	Xe
$6d$	6.471	1.873	2.223	1.349
	2.213	0.763	1.025	0.669
	0.747	0.311	0.473	0.332
	0.273	0.116	0.218	0.165
	0.0998	0.0433	0.100	0.0816
	0.0365	0.0161	0.0463	0.0405
$5f$	4.657	1.325	1.350	1.323
	1.524	0.543	0.656	0.612
	0.689	0.294	0.318	0.283
	0.311	0.159	0.155	0.131
	0.148	0.0862	0.0750	0.0405
$4g$	2.983	1.007	1.207	0.806
	1.224	0.459	0.521	0.369
	0.502	0.209	0.225	0.169
	0.206	0.0954	0.0970	0.0771

Even with these extended basis sets, basis-set superposition errors are non-negligible, and we had to apply a counterpoise (CP) correction.[14] For the determination of the two-body increment $\Delta\epsilon(A,B)$ in Eq. (2), e.g., we calculated the one-body energy $\epsilon(A)$ in the same cluster as $\epsilon(A,B)$, with a ghost basis on position *B*. Similarly, for the three-body increment $\Delta\epsilon(A,B,C)$, Eq. (3), two ghost atoms were used for $\epsilon(A)$, e.g., and one ghost atom for the $\epsilon(A,B)$ involved in $\Delta\epsilon(A,B)$. With basis set *B*, the CP correction amounts to between 22% (Ar) and 43% (Ne) of the dimer binding energy; corresponding values with basis *D* are ~10% (Ar-Xe) and 16% (Ne).

III. RESULTS AND DISCUSSION

A. Rare-gas dimers

Mainly as a test for our basis sets, we determined the equilibrium bond lengths and dissociation energies of the rare-gas dimers (see Table II). For basis set *C*, our results are very similar to those of Burda *et al.*[5] and Runeberg and Pyykkö.[15] Comparing these results with ''exact'' data,[16] which are derived from semiempirical model potentials fitted

TABLE II. Equilibrium bond lengths R_e [Å] and dissociation energies D_e [μH] for rare-gas dimers evaluated with different basis sets, see the text, at the CCSD(T) level. For comparison, we also give DFT-GGA results (Ref. 3) and, under the heading ''Expt.,'' data from semiempirical model potentials fitted to experimental data.

	Basis *A*	Basis *B*	Basis *C*	Basis *D*	GGA	Expt.
$r_e(\mathrm{Ne}_2)$	3.240	3.170	3.131	3.105	3.085	3.091 [a]
$r_e(\mathrm{Ar}_2)$	4.009	3.865	3.841	3.793	4.027	3.757 [a]
$r_e(\mathrm{Kr}_2)$	4.315	4.160	4.134	4.065	4.355	4.008 [a]
$r_e(\mathrm{Xe}_2)$	4.656	4.500	4.495	4.409		4.363 [a]
$D_e(\mathrm{Ne}_2)$	75.0	101.1	119.9	127.7	205	133.8 [a]
						130.7, . . . ,133.8 [b]
$D_e(\mathrm{Ar}_2)$	238.7	348.3	375.3	415.9	224	453.5 [a]
						444.0 [c]
$D_e(\mathrm{Kr}_2)$	291.0	456.0	514.7	580.9	243	637.1 [a]
						636.4, . . . ,640.9 [d]
$D_e(\mathrm{Xe}_2)$	479.1	694.9	735.6	842.1		893.9 [a]
						871.6, . . . ,895.6 [e]

[a] Reference 16.
[b] Reference 23.
[c] Reference 22.
[d] Reference 24.
[e] Reference 25.

to experimental data, between 90% (Ne) and 82% (Xe) of the dissociation energy is recovered with basis set *C*. Basis set *D* yields uniformly about 94% of the dissociation energy for all of the rare-gas dimers. This shows the large influence of the *g* functions, especially for the heavier dimers. The calculated equilibrium bond lengths become shorter with improving basis-set quality. Whereas for basis set *C* the R_e values are by up to 3% too large, the deviations for basis set *D* are between 0.5% and 1.4% only. Also shown in Table II are the best density-functional theory (DFT) results of Ref. 3, which were obtained with the Perdew-Burke-Ernzerhof[17] GGA functional. The authors of Ref. 3 claim that a large part of the binding is due to atomic overlap and therefore accessible to a density-functional treatment. However, the calculated equilibrium distances are by up to 9% too large, and the dissociation energy, while being too large for Ne, is by a factor of 2.5 too small for Kr. This shows that for the van der Waals interaction there is currently no alternative to using the accurate *ab initio* correlation methods such as CCSD(T) and that extended basis sets including *g* functions are necessary for a quantitative description of the binding of rare-gas dimers.

B. Rare-gas crystals

From the calculation of the dimers, we now switch to our main goal, i.e., the rare-gas crystals. To show the degree of transferability from different clusters to the solid and the rate of convergence with increasing interatomic distance, we have listed individual two-body increments in Table III. These increments have been calculated in two-atom and various three-atom clusters. The difference, with basis set *B*, is 2.2% at most, for the nearest-neighbor increment. For increments further apart, transferability errors are of the same relative size but much smaller in magnitude. The convergence with increasing distance of the two atoms is also shown in Table III. The third-nearest-neighbor increment is $\leq 7\%$ of the nearest-neighbor one, in all cases considered. If we assume that the third-nearest-neighbor increment is purely van der Waals-like and is dominated by the leading C_6/r^6 term, we can extract the van der Waals constant C_6 from it and use it for determining the long-range contribution from two-body increments not calculated explicitly in our approach. The corresponding results also can be found in Table III. It is seen that the long-range estimate amounts to about 80% of the third-nearest-neighbor contribution.

For the two-body increments it was possible to employ basis set *D*. However, for the three-body increments this was not possible due to the drastically increasing computational effort with increasing number of correlated electrons. Only calculations with basis set *B* were feasible for all lattice constants; some test calculations were made with basis set *C*. Whereas the Hartree-Fock part is well converged with basis set *B*, this is not true for the correlation contribution. In order to correct for basis-set errors here, we assume the scaling of the correlation energy with the basis set to be the same for three-body as for two-body increments. We tested the reliability of this scaling for Ne, where we performed CCSD calculations with basis set *C* and compared them with the extrapolated values. For the cohesive energy, the extrapolation works well (errors less than 1%); for the lattice constant, the error is about 0.5%. For the bulk modulus, on the other hand, which is calculated from the second derivative of the energy, the scaling is not as reliable. Thus, we can only discuss qualitative trends for the three-body contributions to the bulk modulus.

After testing the quality of the incremental expansion, we now discuss our final results in comparison with experiment and other theoretical approaches. The measured ground-state properties contain zero-point fluctuations not present in our

TABLE III. Test of transferability and convergence for two-body increments, calculated for various two-atom and three-atom clusters with basis set *B* at a lattice constant near the experimental one: (Ne, 4.45 Å; Ar, 5.3 Å; Kr, 5.65 Å; Xe, 6.1 Å). Energies are given in μH, distances in multiples of the lattice constant *a*. The three-atom clusters are labeled according to their angles. In the last row of each block of the table, the two-atom two-body increment has been multiplied by the weight factor appropriate for the fcc structure. The last row of the table gives estimates for van der Waals contributions from the region beyond third-nearest neighbors, see the text.

Distance	Cluster	Ne	Ar	Kr	Xe
$\frac{1}{\sqrt{2}}$	two atom	−100.86	−332.11	−417.49	−628.76
$\frac{1}{\sqrt{2}}$	three atom, 60°	−101.94	−336.32	−427.03	−640.34
$\frac{1}{\sqrt{2}}$	three atom, 90°	−101.39	−334.03	−421.85	−632.49
$\frac{1}{\sqrt{2}}$	three atom, 120°	−101.52	−333.82	−421.51	−632.05
$\frac{1}{\sqrt{2}}$	three atom, 180°	−101.73	−333.32	−420.34	−633.25
	sum with weight 6	−605.16	−1992.66	−2504.94	−3773.56
1	two atom	−20.63	−78.73	−109.71	−165.28
1	three atom, 90°	−20.85	−79.87	−112.12	−168.82
	sum with weight 3	−61.89	−236.19	−329.13	−495.86
$\sqrt{\frac{3}{2}}$	two atom	−5.85	−21.75	−30.39	−44.89
$\sqrt{\frac{3}{2}}$	three atom, 120°	−5.94	−22.12	−31.22	−46.17
	sum with weight 12	−70.20	−261.00	−364.68	−538.60
	van der Waals	−57.71	−214.66	−300.09	−443.33

calculation. Thus, we have to correct the experimental values in order to obtain proper values for comparison. For the cohesive energy we calculate the zero-point vibrational energy using the Debye model $\frac{9}{8}k_B T_{\text{Debye}}$,[18] where the Debye temperature is taken from Ref. 19. This energy is 267 μH for Ne, 328 μH for Ar, 257 μH for Kr, and 228 μH for Xe. More sophisticated calculations by Aziz and Slaman[20] yield 284 μH for Ar, which gives an indication of the error bars of our estimates. For the lattice constant, we assume the deviation from the linear dependence of the lattice constant with temperature to be due to zero-point fluctuations. The temperature dependence of the lattice constants is taken from Ref. 21. That means that our calculated lattice constants should not be compared with the experimental ones at zero or very low temperatures but have to be compared with the linear extrapolation to zero temperature. These lattice constants are between 2.5% (Ne) and 0.5% (Xe) smaller than the measured ones. The value for Ne is not very reliable (error $\pm 0.5\%$), because the linear part of the expansion curve is very small just before the melting point of the crystal.

Our results for the cohesive energy, the lattice constant, and the bulk modulus are listed in Table IV. The *n*-body increments extracted from *n*-atom clusters have been used, in order to minimize the artifacts of the basis set superposition error for $n=2$; van der Waals estimates for contributions beyond third-nearest neighbors have been included as discussed above. In the first columns we report the two-body contributions calculated with different basis sets. We omit the very poor basis set *A*, because it yields only about 60% of the cohesive energy. With basis set *B*, we obtain about 80% of the cohesive energy, and with increasing basis-set quality, we reach about 100% (basis set *D*). Including the repulsive three-body contributions, the calculated cohesive energies are between 93% and 97% of the ‘‘experimental’’ values. The missing part is mainly due to the limited basis, but, as discussed before, a better description of the zero-point energy could also improve the agreement. The three-body contributions increase significantly from Ne (2.7% of the cohesive energy) to Ar (5.5%) and reach 6.5% for Kr and Xe.

Lattice constants are overestimated by up to 3% with basis set *B*, when the many-body expansion is truncated after the two-body increments. This turns out to be mainly due to basis-set incompleteness, whereas the effect of the three-body increments on the lattice constants is quite small (<0.04 Å). It is interesting, in this connection, to follow trends of different energy contributions to the lattice constant: whereas the Hartree-Fock part of the two-body contributions is purely repulsive, the three-body and four-body self-consistent-field (SCF) contributions tend to reduce the repulsion. (For Xe, e.g., the increments to the interaction

TABLE IV. Cohesive energies E_{coh} [μH] per atom, lattice constants a [Å], and bulk moduli B [kbar] for rare-gas crystals, derived from CCSD(T) increments using different basis sets. For comparison, we list experimental values corrected for zero-point fluctuations, see the text.

	Two-body contributions			+Three body	
	Basis B	Basis C	Basis D	Basis D	Expt.
E_{coh} (Ne)	−800.7	−939.9	−999.0	−971.6	−1002.0 [a]
E_{coh} (Ar)	−2716.4	−2924.6	−3224.3	−3043.4	−3268.0 [b]
E_{coh} (Kr)	−3559.0	−3992.8	−4490.6	−4203.8	−4502.0 [b]
E_{coh} (Xe)	−5372.2	−5659.7	−6474.2	−6060.0	−6239.0 [b]
a (Ne)	4.388	4.336	4.299	4.314	4.35 [c]
a (Ar)	5.354	5.320	5.255	5.284	5.23 [d]
a (Kr)	5.763	5.725	5.631	5.670	5.61 [e]
a (Xe)	6.239	6.228	6.110	6.137	6.10 [f]
				Basis B	
B (Ne)	14.3	17.5	19.0	14.6	10.9 [g]
B (Ar)	26.9	29.2	33.5	27.2	23.8 [h]
B (Kr)	28.1	31.8	37.5	28.6	36.1 [i]
B (Xe)	33.8	34.8	42.4	29.3	36.4 [j]

[a] Reference 26.
[b] Reference 27.
[c] Reference 28.
[d] Reference 29.
[e] Reference 30.
[f] Reference 31.
[g] Reference 32.
[h] Reference 33.
[i] Reference 34.
[j] Reference 35.

energy near the experimental lattice constant are 6500 μH, −400 μH, and −96 μH, respectively.) When the correlation contributions are added, a minimum in the energy curve develops with the two-body terms, which is shifted to larger distances when three-body correlation terms are added. At the highest level (basis set D, three-body terms included), our results for the lattice constants are too small for Ne and up to 1% too large for the other crystals. The deviation from experiment for Ne may well be due to the poor estimate of the zero-point fluctuations in this case, since further extension of the basis is expected to decrease (rather than increase) the calculated value of the lattice constant. Higher-order contributions than three-body ones can be estimated to have only a very small influence on the lattice constants.

In the calculation for xenon, we applied the core-polarization potential in order to account for core-valence correlation involving mainly the outer-core $4d$ shell of the Xe atom. We find that the CPP decreases the lattice constant by about 1% and enhances the cohesive energy by about 500 μH. This is certainly an upper bound to the true core-polarization effect, due to mixing in of small static contributions for the clusters, which would be absent for the bulk. Nevertheless, the numbers show that even for krypton core-valence-correlation contributions (from the $3d$ shell) might have a non-negligible influence on cohesive energy and lattice constant. A rough estimate of the magnitude can be obtained from the X^{8+} core dipole polarizability, which for X $=$Kr is about a quarter of the Xe value.

For bulk moduli, we did not correct the experimental values for zero-point fluctuations (which should increase their magnitude); it is difficult to achieve reliable numbers with a simple estimate—a full quantum-mechanical treatment would be necessary here. Therefore, we shall only discuss trends. With increasing basis-set quality, the bulk moduli increase (since lattice constants become shorter). The three-body contributions (the values in Table IV refer to basis set B, i.e., no extrapolation to basis set D has been attempted) have virtually no influence. In comparison with uncorrected experimental values all of our calculated bulk moduli are too large.

Finally, we want to compare our results with the Ar crystal data published by Lotrich and Szalewicz.[6] For the two-body contributions, which cover the main part of the bonding, these authors used a model potential fitted to experiment, and only the three-body contributions were calculated by *ab initio* methods. Using the model potential of Aziz[22] based on dimer data, they obtain a two-body energy of 3459 μH, 7% higher than our value. This is a good estimate of the error due to the limited basis set in our *ab initio* calculation. For the three-body contributions, Lotrich and Szalewicz applied symmetry-adapted perturbation theory (SAPT). Their result is 15% larger in magnitude than our three-body term, and it leads to an increase of the lattice constant by 0.04 Å as compared to a corresponding value of 0.03 Å in our work.

IV. CONCLUSION

We have used a many-body expansion of the interaction energy to determine cohesive energies, lattice constants, and bulk moduli of the rare-gas crystals neon, argon, krypton, and xenon, in the experimental dense-packed fcc structure. In a first step, pair interaction energies were calculated at the CCSD(T) level, using relativistic energy-consistent pseudopotentials together with extended basis sets. Including, in a next step, corrections involving triples of atoms, we recover about 95% of the experimental cohesive energy, while calculated lattice constants are accurate within ±1%. As expected, the importance of three-body contributions increases from Ne (∼3%) through Xe (∼7%), showing that the heavier rare-gas crystals cannot be accurately described with purely two-body forces. The present results for van der Waals crystals are of the same accuracy as our previous calculations for ionic crystals and semiconductors.

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