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Comparison of the incremental and hierarchical methods for crystalline neon

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Abstract
We present a critical comparison of the incremental and hierarchical methods for the evaluation of the static cohesive energy of crystalline neon. Both of these schemes make it possible to apply the methods of molecular electronic structure theory to crystalline solids, offering a systematically improvable alternative to density functional theory. Results from both methods are compared with previous theoretical and experimental studies of solid neon and potential sources of error are discussed. We explore the similarities of the two methods and demonstrate how they may be used in tandem to study crystalline solids.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Electronic structure studies of crystalline solids are dominated by density functional theory (DFT), but with conventional local, gradient corrected or hybrid functionals, these have a number of short-comings. The calculations lack a description of long-range dispersion; and they suffer from spurious self-interaction terms, leading to an assortment of problems ranging from underestimation of reaction barriers [1] to improper description of solid surfaces (see for example [2]). Perhaps most seriously there is no clear route for systematic improvement of accuracy.

A number of wavefunction-based methods have been developed to model crystalline solids, including quantum Monte Carlo (QMC; see for example [3]) and techniques that extend quantum chemical electronic structure methods to include periodic boundary conditions. Work in the latter category has mainly focused on periodic MP2 implementations, including the Laplace-transform atomic-orbital driven implementation of Ayala *et al* [4]; the local, density fitted method in the CRYSCOR code [5, 6]; and the plane-wave implementation developed in VASP [7].

An alternative is offered by methods which seek to address the electron correlation problem in solids using molecular electronic structure calculations on fragments. This has been possible for a long time through the incremental scheme (or method of increments) [8–10] and, more recently, by the hierarchical method [11, 12]. The chief advantage of such schemes over full periodic implementations is their simplicity, and the straightforward extension to more advanced electronic structure methods. In the present work, each scheme will be briefly reviewed, then their performance compared for the computation of the cohesive energy of crystalline neon.

Due to the importance of dispersion in the bonding of neon, DFT results are completely unreliable, and the spurious effects that lead to binding obviously depend strongly on the exchange–correlation functional used [13]. Rościszewski *et al* demonstrated that by applying molecular electronic structure techniques using the incremental scheme it is possible to reproduce the experimental cohesive energy [14] to high accuracy.

Neon forms a face-centred-cubic crystal, with the empirically determined equilibrium lattice parameter $a = 4.35$ Å [14]. This value was obtained from the directly observed lattice parameter [15] by extrapolation to 0 K and subtraction of zero-point effects. Only the correlation component of the cohesive energy will be discussed here. The empirical static cohesive energy is $-1002\ \mu E_\mathrm{h}$, again obtained from experimental values [16] by subtraction of zero-point effects in [14]. The Hartree–Fock approximation to the cohesive energy is known to be $+685\ \mu E_\mathrm{h}$ [17] and therefore the correlation contribution to the cohesive energy should amount to $-1687\ \mu E_\mathrm{h}$.

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2. Incremental method

One of the most general techniques for dealing with an ensemble of many interacting particles is the many-body expansion. Applied to a crystalline solid the individual low-order terms of the expansion can be computed using molecular electronic structure theory. This so-called incremental method is described in detail in a recent review [18]. A brief outline of the method as used in this work is given below.

The binding energy of a finite cluster of m atoms, relative to free atoms, can be expanded exactly as the sum of all the interactions between the constituent atoms:

$$E_{\text{bind}} = \sum_{i<j}^{m} \epsilon_{ij} + \sum_{i<j<k}^{m} \epsilon_{ijk} + \cdots + \epsilon_{ijk\cdots m}, \tag{1}$$

where the indices $i, j, \ldots$ refer to atoms. The interaction energies can be determined by calculating the energy of all the indexed atoms at the same geometry as they are found in the cluster, and subtracting the relevant lower-order terms. In this way the two-body interaction can be written as

$$\epsilon_{ij} = E_{ij} - \epsilon_i - \epsilon_j, \tag{2}$$

where E_{ij} is the energy of the two-atom combination and ϵ_i and ϵ_j are the individual atomic energies. Equation (1) is of course exact, but the expansion is useful only because high-order (many-atom) terms become successively smaller, and can be approximated or neglected without introducing significant errors in the total energy.

A similar concept may be applied to an infinite lattice of atoms. The static cohesive energy per atom can be found by selecting one atom, indexed as 1, and summing its interactions with the other atoms in the crystal:

$$E_{\text{coh}}^{\text{static}} = \frac{1}{2}\sum_{1<j}^{\infty} \epsilon_{1j} + \frac{1}{3}\sum_{1<j<k}^{\infty} \epsilon_{1jk} + \cdots. \tag{3}$$

As before, higher-order terms which involve many atoms tend to be negligibly small and this allows the summation to be truncated. As the distances between atoms become large the interaction energies decrease systematically, and cutoffs can be applied.

3. Hierarchical method

The hierarchical method [11] is an alternative way to apply molecular electronic structure techniques to solid-state systems. The method extrapolates correlation energies of small clusters of atoms to the correlation component of binding in the infinite crystal. This is achieved by careful subtraction of edge effects, and provides additional information about the crystal, including surface formation energies. The method has been demonstrated to achieve very high levels of accuracy for the ionic crystal lithium hydride [11, 12].

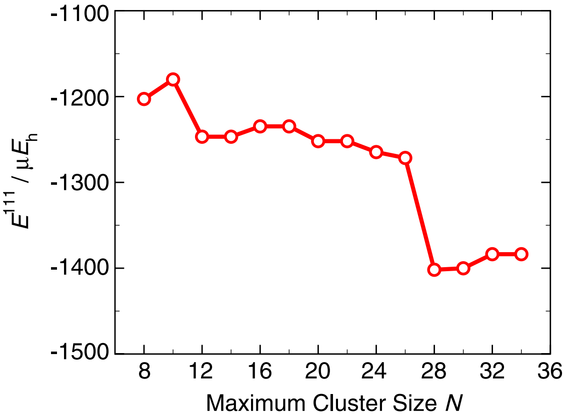

Figure 1. E^{111} as a function of maximum cluster sizes N. Correlation contributions to binding energies were calculated using DF-MP2/aug-cc-pVTZ.

The correlation component of the binding energy for a finite cluster, labelled by the number of atoms along each lattice vector $(l \times m \times n)$, can be written in the form

$$\begin{aligned}\Delta E_{lmn}^{\text{corr}} = {} & 8E^{000} \\ & + 4[(l-2)E^{001} + (m-2)E^{010} + (n-2)E^{100}] \\ & + 2[(l-2)(m-2)E^{011} + (l-2)(n-2)E^{101} \\ & \qquad + (m-2)(n-2)E^{110}] \\ & + (l-2)(m-2)(n-2)E^{111}.\end{aligned} \tag{4}$$

The energy quantities give the correlation contributions to the binding energy from atoms at the corners (E^{000}), edges (e.g. E^{001}), surfaces (e.g. E^{011}) or in the interior of the crystal (E^{111}). The numerical factors simply specify the number of atoms in each of these environments in the cluster of $l \times m \times n$ atoms. There are eight unknown parameters in the equation, so by computing the correlation contributions to binding energies of eight distinct clusters, one can solve equation (4) to obtain, amongst other terms, the bulk-like quantity E^{111}. In the limit of infinite cluster sizes, E^{111} gives the correlation contribution to the cohesive energy.

In common with previous studies [11, 12], symmetry arguments allow one to reduce the number of unknown energy terms, and thereby the number of required clusters, to four. For a given maximum number of atoms in a cluster, N, the possible clusters were listed lexicographically and the four clusters nearest to the end of the list were chosen, subject to the simultaneous equations being soluble.

4. Hierarchical results

If the electron correlation effects are sufficiently short ranged then the calculated value of E^{111} should converge rapidly with maximum cluster size N. The results for E^{111} using density fitted second-order Møller–Plesset perturbation theory (DF-MP2) in the aug-cc-pVTZ basis set are shown in figure 1. All calculations have been performed using the Molpro electronic structure package [19].

There are two significant jumps in the value of E^{111} as N increases. These coincide with the elimination of certain types of cluster in the calculations. At $N = 8$ the clusters chosen include chains, sheets and a parallelepiped. By $N = 12$ only

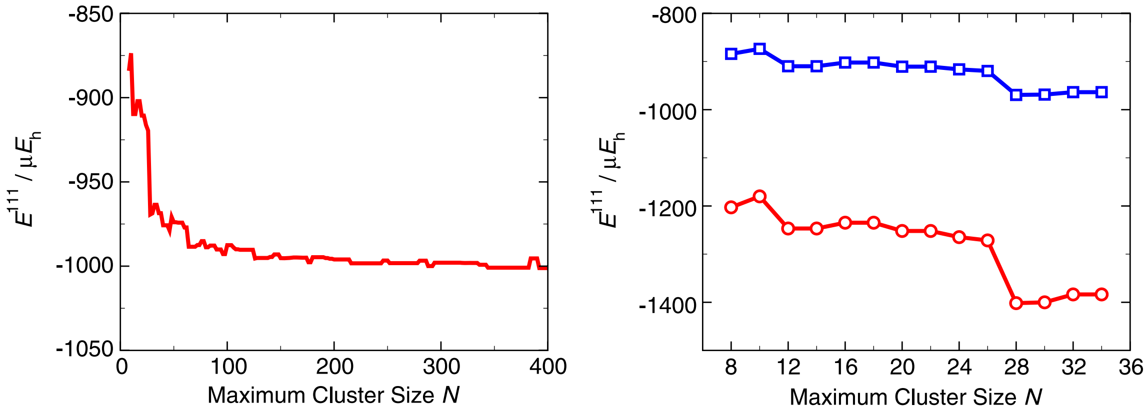

Figure 2. Convergence of E^{111} with increasing maximum cluster size N. All correlation energies calculated using MP2/aug-cc-pVTZ. On the left, the 2-body hierarchical results are shown to large maximum N; on the right the full (circles) and two-body (squares) hierarchical results are compared.

sheets and parallelepipeds are used and from $N = 28$ only parallelepipeds are chosen. Clearly those clusters which are most 'bulk-like' will give a better description of the physics of the crystal. It is necessary at very small cluster sizes to include chains and sheets of atoms in order to have enough different cluster geometries to solve the simultaneous equations.

Further jumps would be expected as clusters with particular smallest dimensions are eliminated: for example at $N = 64$ all of the clusters chosen will have $l, m, n > 2$. It is not straightforward to perform quantum-mechanical calculations on clusters this large, but it would nevertheless be reassuring to be able to study the convergence of the hierarchical scheme to very large cluster sizes. For this purpose, the correlation energy of each cluster relative to atoms can be approximated as a many-body expansion truncated at second order. The correlation component of the binding energy at each interatomic separation is then calculated using counterpoise corrected MP2/aug-cc-pVTZ. The energy of the cluster can then be written as

$$E_{lmn} = \sum_d n_d V(d), \tag{5}$$

with the summation running over all interatomic distances d that appear $n_d > 0$ times in the cluster. For example the two-body approximation to the binding energy of the $2 \times 2 \times 2$ cluster is

$$E_{222} = 18V(a/\sqrt{2}) + 3V(a) + 6V(\sqrt{3/2}a) + V(\sqrt{3}a). \tag{6}$$

Solving the simultaneous equations (equation (4)) as before, values for $N = 8$–400 were collected. These results are illustrated in figure 2 and the errors associated with truncating after each jump are shown in table 1. These results suggest that in order to achieve high accuracy for neon, quite large cluster sizes would need to be considered (at least 64 atoms to reduce errors to about 1%).

The two-body expansion of the cluster energies also allows us greater insight into how the hierarchical method works. By solving equation (4) one obtains E^{111} as a simple linear combination of energies of different clusters.

Table 1. Magnitude of jumps in E^{111} ($|\delta E^{111}|$) at particular values of N and the error associated with truncation at that cluster size, |error|, relative to $N = 400$. E^{111} calculated using two-body approximation and interaction energies calculated with MP2/aug-cc-pVTZ. All energies are quoted in μE_h.

N	$\lvert\delta E^{111}\rvert$	|error|
12	36.09	91.4
28	49.80	32.5
64	11.43	12.6
126	5.15	6.0
216	2.56	2.9
344	1.71	0.2

Approximating the energy of each cluster by the two-body expansion, one can then express E^{111} as a linear combination of the various pair interactions $V(d)$ at the different interatomic distances d represented in the crystal. The coefficients for each $V(d)$ contribution then can be computed, and it is both instructive and entertaining to do so. The results are shown in table 2.

As the maximum cluster size N increases the number of coefficients in the hierarchical solutions which match those in the standard two-body expression (equation (5)) increases. Later terms in the expansion will contribute very little to the cohesive energy as the interaction distance becomes large. Each jump in the hierarchical results can be matched to a change in the number of matching coefficients. Most interestingly, the careful subtraction of edge effects in the hierarchical method leads to correct numbers of neighbours (for example, 12 nearest neighbours) even when there is no atom in this environment in any of the clusters used. For example, at $N = 8$ there are no atoms with 12 nearest and six next-nearest neighbours; yet the two-body hierarchical energy expression with $N = 8$ reproduces these first two coefficients.

By comparing the hierarchical results using the two-body approximation to the full hierarchical results, it is clear that higher-order terms and counterpoise correction effects are important (see figure 2). In neglecting higher-order terms, the two-body expansion consistently underestimates E^{111}. Nevertheless by applying a correction based on the two-body

Table 2. Coefficients for contributions at each possible interatomic distance in the crystal to E^{111} values computed at particular maximum cluster sizes N using the two-body approximation to cluster energies. It can be seen that as N increases the number of coefficients that agree with the bulk n_d increases. (For clarity those which agree are shown in bold.)

d/a:	$1/\sqrt{2}$	1	$\sqrt{3/2}$	$\sqrt{2}$	$\sqrt{5/2}$	$\sqrt{3}$	$\sqrt{7/2}$	2	$3/\sqrt{2}$	$\sqrt{5}$	$\sqrt{11/2}$
$N = 12$	**6**	**3**	5	−1	2	1	−2	0	−3	0	1
$N = 28$	**6**	**3**	**12**	**6**	**12**	$-\frac{3}{2}$	$-\frac{15}{2}$	3	$-\frac{21}{4}$	−5	$\frac{15}{4}$
$N = 64$	**6**	**3**	**12**	**6**	**12**	**4**	**24**	**3**	**18**	**12**	$-\frac{32}{3}$
n_d	6	3	12	6	12	4	24	3	18	12	12

Table 3. Hierarchical result for E^{111} at $N = 34$ using DF-MP2/aug-cc-pVTZ and corrections to that value based on calculations using different methods, basis sets and cluster sizes. All values quoted in μE_h. AVTZ is used as an abbreviation for aug-cc-pVTZ, and AV[T,Q]Z for results with cubically extrapolated correlation energies using the corresponding triple-zeta and quadruple-zeta basis sets (see [20]).

Term	N	E^{111}
DF-MP2/AVTZ	34	−1383.68
2-body DF-MP2/AVTZ	400	−37.56
DF-MP2/AV[T,Q]Z	8	−111.01
CCSD(T)/AVDZ	8	−218.47
$E_\mathrm{coh}^\mathrm{corr}$		−1750.72
$E_\mathrm{coh}^\mathrm{corr}$ [14, 17]		−1687

Table 4. Correlation energy of the 2 × 2 × 2 cluster using DF-MP2/aug-cc-VTZ with different levels of CP correction. No CP indicates that no BSSE correction was used. Normal CP indicates that interactions energies were calculated as in equation (7). Full CP indicates that all interaction energies were calculated in the basis of the 2 × 2 × 2 cluster. All energies quoted are in E_h.

Contribution	No CP	Normal CP	Full CP
1-body	−2.179 511	−2.179 511	−2.180 325
2-body	−0.003 432	−0.002 572	−0.002 645
3-body	+0.000 023	+0.000 006	+0.000 006
4-body	−0.000 083	+0.000 000	+0.000 000
5-body	+0.000 050	+0.000 000	+0.000 000
6-body	−0.000 011	+0.000 000	+0.000 000
E_total	−2.182 964	−2.182 077	−2.182 964
$E_\mathrm{coh}^\mathrm{a}$	−0.003 453	−0.002 572	−0.003 453

[a] Calculated relative to atoms without CP.

Table 5. Correlation contributions from the incremental method to the cohesive energy calculated using MP2/aug-cc-pVTZ in μE_h. Results are given without BSSE correction (no CP) and with a counterpoise correction as defined in equation (7) (normal CP). The final row includes values corrected using the hierarchical basis set and coupled-cluster corrections from table 3.

Incremental term	No CP	Normal CP
2-body	−1312	−1002
3-body	−72	+7
4-body	−108	+0
E_coh	−1492	−995
E_coh (corr.)	−1821	−1324

results it should be possible to reduce some of the error associated with using small cluster sizes in the full hierarchical calculations.

It has been shown previously that the difference between hierarchical results using methods is to a good approximation constant with cluster size [12]. This allows a series of corrections to be computed using smaller maximum cluster sizes, which can be added to the DF-MP2/aug-cc-pVTZ results to improve accuracy. The results of these calculations are shown in table 3, where it can be seen that the best estimate of the correlation component of the cohesive energy is within 100 μE_h of the reference value. This error could be systematically reduced by improving the basis sets used for the correction terms; by performing calculations at higher values of N; and by accounting for the effects of core correlation and correlation beyond the CCSD(T) approximation.

5. Incremental results

In order to compare the results of the hierarchical and incremental methods both sets of calculations must be performed using the same basis set and method. Another factor which needs to be considered is the treatment of basis set superposition error (BSSE) in both methods. By correcting for BSSE the incremental method can be converged using fewer terms, however the hierarchical method employs no corrections for this effect. As larger basis sets are used, the infinite basis set limit is approached and the effect of BSSE vanishes.

The correlation energy of the 2 × 2 × 2 cluster relative to free atoms (computed in the atomic basis set) was found to be −3453 μE_h using DF-MP2/aug-cc-pVTZ. This was also calculated using the incremental method in three different ways: with no BSSE correction, with a normal counterpoise (CP) correction [21] and with a full counterpoise correction. In the last case, each increment is evaluated in the basis of the full cluster [22]; both normal CP and full CP corrections have been implemented in many-body expansions previously [23].

The results are shown in table 4. Without correcting for BSSE the incremental terms do not converge, even when the expansion includes 6-body terms. This poor convergence is also observed in the calculation of the bulk cohesive energy (see table 5). The total energy and cohesive energy of the cluster are reproduced accurately however. Both methods which correct for BSSE converge rapidly but to different values. The many-body expansion using the full CP correction gives the correct cohesive energy, but the normal CP correction does not. Only in the infinite basis set limit would the normal CP corrected incremental result be exact. The reason for this discrepancy can be seen clearly from the expression for the total energy of a dimer:

$$E_{\text{total}}^{\text{dimer}} = E_{\text{A}} + E_{\text{B}} + [E_{\text{AB}} - E_{\text{A}}(\text{AB}) - E_{\text{B}}(\text{AB})] \qquad (7)$$

where $E_{\text{A}}(\text{AB})$ is the energy of atom A calculated in the basis of both atoms. Only if $E_{\text{A}} = E_{\text{A}}(\text{AB})$ and $E_{\text{B}} = E_{\text{B}}(\text{AB})$ would $E_{\text{AB}} = E_{\text{total}}^{\text{dimer}}$, and this would only generally be the case in the infinite basis set limit. The calculation of the full CP correction for systems with large numbers of atoms becomes computationally intensive. Therefore the normal CP correction was applied to find the cohesive energy by the incremental method.

Without the CP correction, the convergence is poor, although the result summed up to 4-body terms is quite close to the analogous hierarchical number. On the other hand, with the CP correction the convergence is excellent, but the result lies some ∼400 μE_{h} from the hierarchical value at the same level of theory. The hierarchical result, however, does not account for BSSE. When the correlation energies of the hierarchical clusters are determined using the counterpoise corrected two-body energies, the cohesive energy at $N = 400$ is found to be $-1001\ \mu E_{\text{h}}$, in excellent agreement with the full two-body energy, $-1002\ \mu E_{\text{h}}$. The incremental results can be corrected using the basis set and coupled-cluster corrections from table 3; these data are also presented in table 5. It can be seen that the non-CP corrected result ($-1821\ \mu E_{\text{h}}$) agrees quite well with the hierarchical ($-1751\ \mu E_{\text{h}}$) and accurate ($-1687\ \mu E_{\text{h}}$) results, albeit with questionable convergence. The corrected incremental result using CP corrections, $-1324\ \mu E_{\text{h}}$, is well converged but some considerable way removed from the other data. This may arise from the pathological sensitivity of the cohesive energy of the neon crystal to BSSE effects, and, as noted earlier, the discrepancy would most certainly fall if the basis sets were extended.

6. Conclusions

We have computed the correlation component of the cohesive energy of crystalline neon by applying molecular electronic structure methods in two different ways. We have shown that the accuracy of the hierarchical method can be understood by the observation that even using clusters that have no atoms in the bulk interior, the method correctly describes the interactions of a bulk atom with its 12 nearest and six next-nearest neighbours.

Both the hierarchical and incremental schemes can be used to treat electron correlation in bulk neon, and using the relatively simple methods applied here, agreement with an experimentally derived reference value is on the order of 100 μE_{h}. But the study has highlighted that both methods have drawbacks, and can therefore be applied in a complementary way. To converge the hierarchical correlation energy for crystalline neon to within 1% one would have to use clusters of at least 64 atoms, presenting a challenge for conventional molecular electronic structure methods. On the other hand, in small basis sets basis set superposition error makes the incremental scheme challenging: without counterpoise corrections, the scheme converges slowly; and with counterpoise corrections it converges smoothly, but to a different answer.

Further investigations will be made into the relationship between the methods and in particular we will pursue the idea of using low-order many-body expansions to improve convergence of the hierarchical scheme with respect to the number of atoms treated.

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