

Extension of molecular electronic structure methods to the solid state: computation of the cohesive energy of lithium hydride

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Received 20th September 2006, Accepted 2nd October 2006

First published as an Advance Article on the web 10th October 2006

DOI: 10.1039/b613676a

We describe a simple strategy for calculating the cohesive energy of certain kinds of crystal using readily available quantum chemistry techniques. The strategy involves the calculation of the electron correlation energies of a hierarchy of free clusters, and the cohesive energy E_{coh} is extracted from the constant of proportionality between these correlation energies and the number of atoms in the limit of large clusters. We apply the strategy to the LiH crystal, using the MP2 and CCSD(T) schemes for the correlation energy, and show that for this material E_{coh} can be obtained to an accuracy of ~ 30 meV per ion pair. Comparison with the experimental value, after correction for zero-point energy, confirms this accuracy.

Over the past 20 years, the study of condensed-matter electronic structure has been dominated by Density Functional Theory (DFT) owing to its high efficiency, rapid basis-set convergence and relatively high accuracy. However, a systematically improvable treatment of electron correlation within DFT has proved elusive. Quantum chemistry, by contrast, traditionally emphasises the systematic treatment of correlation, and successful hierarchies have been established based on Møller–Plesset and coupled cluster theory. Such quantum chemical methods would make a huge impact in the study of condensed matter, and a variety of approaches have been developed. These include the local ansatz for coupled cluster treatments, developed by Stollhoff and Fulde;¹ AO-driven Laplace-transform MP2;² Stoll's method of increments;³ and the local ansatz of Pulay and Saebø.^{4,5} For a recent review, see ref. 6. A comparison of the relative merits of these methods and our own is beyond the scope of the present Communication.

We present here a simple strategy for calculating the cohesive energy of an infinite crystal, using readily available quantum chemistry methods. The method can, in principle, be applied to any crystal, but we describe it for an ionic solid MX (M = cation, X = anion) with the rock salt structure. We work with orthorhombic $l \times m \times n$ blocks of crystal with all ions fixed on bulk lattice positions and lmn even. With E_{lmn}^{tot} being the total energy of the block relative to isolated atoms, the cohesive energy $E_{\text{coh}}^{\text{static}}$ of the static crystal per ion pair is the limit of $2E_{lmn}^{\text{tot}}/lmn$ as l , m and n all tend to infinity. The cohesive energy of the real material at $T = 0$ K is obtained

by adding the zero-point vibrational energy per ion pair: $E_{\text{coh}}^{0\text{K}} = E_{\text{coh}}^{\text{static}} + E_{\text{zp}}$.

We decompose E_{lmn}^{tot} into its Hartree–Fock and correlation parts:

$$E_{lmn}^{\text{tot}} = E_{lmn}^{\text{HF}} + E_{lmn}^{\text{corr}} \quad (1)$$

The limit of $2E_{lmn}^{\text{HF}}/lmn$ as l , m and $n \rightarrow \infty$ is the Hartree–Fock approximation to the cohesive energy of the static crystal, which can be calculated by standard methods. We now express the correlation energy of the block E_{lmn}^{corr} as the sum of the correlation energy of the MX molecules plus a remainder, which we term the ‘correlation residual’, $\Delta E_{lmn}^{\text{corr}}$:

$$E_{lmn}^{\text{corr}} = \frac{1}{2}lmn E_{\text{mol}}^{\text{corr}} + \Delta E_{lmn}^{\text{corr}} \quad (2)$$

The correlation energy $E_{\text{mol}}^{\text{corr}}$ of the MX molecule, relative to that of isolated atoms, refers to an internuclear separation equal to that in the crystal. This can be computed very accurately, so that the only difficult part of the cohesive energy is the limit involving the correlation residual $2\Delta E_{lmn}^{\text{corr}}/lmn$ as l , m and $n \rightarrow \infty$.

For blocks $l \times m \times n$ with fixed l and m , the correlation residual $\Delta E_{lmn}^{\text{corr}}$ has the asymptotic form

$$\Delta E_{lmn}^{\text{corr}} = c_{lm}^0 + c_{lm}^1 n \quad (3)$$

as $n \rightarrow \infty$, where c_{lm}^z are constant coefficients. We shall show below that this asymptotic form is rapidly attained in practice. For fixed l , the coefficients c_{lm}^z themselves become linear in m for large m :

$$c_{lm}^z = c_l^{z0} + c_l^{z1} m, \quad (4)$$

and similarly:

$$c_l^{z\beta} = c^{z\beta 0} + c^{z\beta 1} l. \quad (5)$$

Substituting eqn (4) and (5) into eqn (3), and using the cubic crystal symmetry, we obtain:

$$\Delta E_{lmn}^{\text{corr}} = c^{000} + c^{001}(l+m+n) + c^{011}(lm+ln+mn) + c^{111}lmn \quad (6)$$

for the correlation residual energy in the limit of large l , m , n . We see from eqn (6) that the contribution of the correlation residual to the cohesive energy per ion pair is $2c^{111}$.

The limiting processes just described give one way of determining c^{111} , and hence the correlation residual part of the cohesive energy. However, we have developed a more automatic and general procedure that allows the convergence with respect to block size to be studied in more detail. If we

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have four distinct blocks $l_i \times m_i \times n_i$ ($i = 1, 2, 3, 4$), then their residual correlation energies $\Delta E_{l_i m_i n_i}^{\text{corr}}$, when inserted on the left of eqn (6), give four simultaneous equations that can be solved to obtain estimates for the four asymptotic coefficients c^{000} , c^{001} , c^{011} and c^{111} , provided the equations are linearly independent. The accuracy of the estimates can be improved by repeating the procedure for larger blocks. In our ‘hierarchical algorithm’, we generate groups of four blocks as follows: for a positive integer N , we construct the list of unique blocks with even lmn and with $lmn \leq N$. The list is ordered lexicographically, so for example for $N = 8$, the list is (1,1,2), (1,1,4), (1,1,6), (1,1,8), (1,2,2), (1,2,3), (1,2,4), (2,2,2). We take the last four blocks in the list, subject to solubility of the simultaneous equations, and solve to yield a value of c^{111} . This estimate converges to the exact value as $N \rightarrow \infty$. The ordering of the list is important, since it ensures that the groups of four contain the most ‘bulk-like’ blocks.

Our calculations on LiH were performed with the latest version of the Molpro code.⁷ We have used density fitting to accelerate many of our calculations, with standard fitting sets.⁸ Errors relative to the corresponding exact methods are very small (e.g. 6 μE_h difference in the MP2/cc-pVTZ total energy of the LiH molecule with and without density fitting). The results we report all refer to the experimental lattice parameter $a_0 = 4.084 \text{ \AA}$.

We discuss first the asymptotic behaviour of the correlation residual energy E_{lmn}^{corr} as l, m and $n \rightarrow \infty$. Fig. 1 shows the dependence of $\Delta E_{lmn}^{\text{corr}}$ on n for fixed values of l and m , calculated at the MP2/cc-pVTZ level, with frozen cores. (To examine the asymptotes of $\Delta E_{lmn}^{\text{corr}}$, the same basis set must be used for all l, m and n .) The results show that the correlation residual energy is small ($\Delta E_{lmn}^{\text{corr}}/lmn \sim 6 \text{ m}E_h$), and that the asymptotic linear form (eqn 3) is rapidly attained. We have applied our ‘hierarchical algorithm’ up to $N = 64$ at the MP2/cc-pVTZ level with frozen cores. The estimated values of the c^{111} coefficient for a sequence of N values are shown in Fig. 2. There are irregularities at smaller N values, where chains and sheets, rather than bulk-like blocks, are used, but the uncertainty in the estimated value of c^{111} for $n \rightarrow \infty$ is much less than 1 $\text{m}E_h$. Corrections for core correlation (MP2(full)/cc-pCVTZ), basis-set incompleteness (MP2/cc-pVQZ) and higher levels of correlation (CCSD(T)/cc-pVTZ) were computed using the hierarchical algorithm up to $N = 16$. Our MP2/

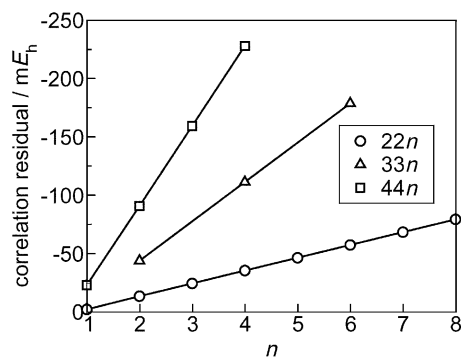


Fig. 1 Correlation residuals $\Delta E_{lmn}^{\text{corr}}$ of LiH blocks of increasing sizes computed at the frozen-core MP2/cc-pVTZ level. Note the rapid convergence to linear form.

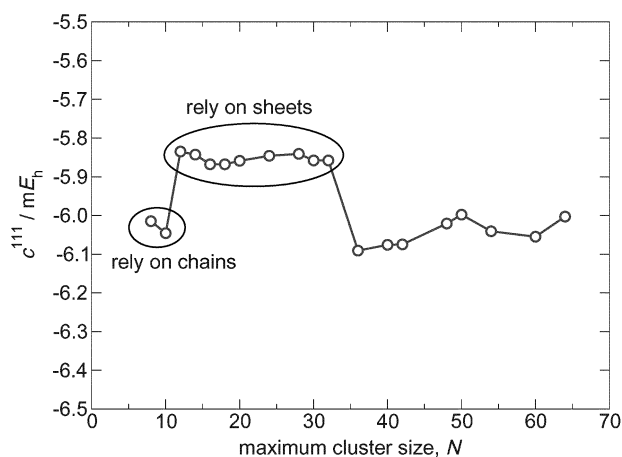


Fig. 2 Correlation residual contribution c^{111} (MP2/cc-pVTZ) to cohesive energy of the LiH crystal computed using the hierarchical algorithm (see text) for a sequence of maximum clusters sizes N .

cc-pVTZ result for c^{111} and the corrections to this result are reported in Table 1.

To obtain the total correlation energy of the LiH crystal per ion pair, we add to $2c^{111}$ the correlation energy of the LiH molecule ($r_{\text{LiH}} = 2.042 \text{ \AA}$) relative to that of isolated atoms. The correlation energies of the LiH molecule and Li atom were computed using all-electron FCI/cc-pCVTZ, giving $E_{\text{mol}}^{\text{corr}} = -36.4 \text{ m}E_h$. We obtain a basis-set correction by applying the cubic extrapolation to CCSD(T)/cc-pCVTZ and cc-pCVQZ correlation energies. This provides an estimate of $-1.9 \text{ m}E_h$ for the basis set incompleteness of the FCI result, giving our final estimate $E_{\text{mol}}^{\text{corr}} = -38.4 \text{ m}E_h$.

The final part of the static cohesive energy $E_{\text{coh}}^{\text{static}}$ is the HF contribution $E_{\text{coh}}^{\text{HF}}$, for which there is a literature value of $-130 \text{ m}E_h$.⁹ This value was obtained by the questionable procedure of taking the difference between a restricted basis (EBS) energy of the crystal and the HF basis set-limit for the isolated atoms. EBS does not have functions to represent the 2s orbital of Li, so here we first compute the cohesive energy relative to free ions. The diffuse nature of H^- is carried in the crystal by basis functions on neighbouring sites. We therefore computed the energy of H^- in the EBS basis for blocks of LiH up to $3 \times 5 \times 5$, with the hydride on the central site. The resulting cohesive energy with respect to free ions was converted to the atomic

Table 1 Contributions to the cohesive energy $E_{\text{coh}}^{\text{OK}}$ of the LiH crystal relative to isolated atoms and comparison with experiment (see text)

Contribution	Energy/ $\text{m}E_h$
$E_{\text{coh}}^{\text{HF}}$	-134.4
$E_{\text{mol}}^{\text{corr}}$	-38.4
$2c^{111}$ ref. ^a	-12.0
$2c^{111}$ core. ^b	2.2
$2c^{111}$ CCSD(T) ^c	-1.0
$2c^{111}$ Basis ^d	-0.2
E_{zp}	7.8
$E_{\text{coh}}^{\text{OK}}$ (calc.)	-176.0
$E_{\text{coh}}^{\text{OK}}$ (exp.)	-175.0

^a MP2/cc-pVTZ. ^b MP2(full)/cc-pCVTZ – MP2/cc-pVTZ. ^c CCSD(T)/cc-pCVTZ – MP2/cc-pVTZ. ^d MP2/cc-pVQZ – MP2/cc-pVTZ.

reference using the HF basis limit energies of Li^+ , Li , H^- and H , to obtain $E_{\text{coh}}^{\text{HF}} = -134.4 \text{ m}E_{\text{h}}$.

It suffices to obtain the zero-point energy E_{zp} from DFT phonon frequencies, which for semi-ionic materials like LiH are generally correct to better than 5%. We calculated phonon dispersion relations by the linear-response and small displacement methods,¹⁰ using the VASP and ESPRESSO codes.¹¹ Results in the local-density and generalised-gradient approximations were $E_{\text{zp}} = 7.6$ and $7.8 \text{ m}E_{\text{h}}$, respectively.

The contributions to our final value for the zero-temperature cohesive energy are presented in Table 1, and we obtain $E_{\text{coh}}^{\text{OK}} = -176.0 \text{ m}E_{\text{h}}$. The enthalpy of formation of LiH crystal from a Li crystal and H_2 gas at standard conditions ($T = 298.15 \text{ K}$, $P = 1 \text{ bar}$) has been determined by several techniques, and the JANAF Tables¹³ list five experimental values, which are consistent to within $\sim 0.3 \text{ kcal mol}^{-1}$ ($\sim 0.5 \text{ m}E_{\text{h}}$). We use here the value $-21.66 \text{ kcal mol}^{-1}$ from the middle of the range. To obtain from this the $T = 0 \text{ K}$ cohesive energy, we use the JANAF values for (a) the enthalpy difference of a LiH crystal between $T = 0 \text{ K}$ and $T = 298.15 \text{ K}$; (b) the enthalpy of formation of Li gas from a Li crystal under standard conditions; (c) the enthalpy difference of H_2 gas between $T = 0 \text{ K}$ and $T = 298.15 \text{ K}$; (d) the dissociation energy of the H_2 molecule. This yields the experimental value for the $T = 0 \text{ K}$ cohesive energy $E_{\text{coh}}^{\text{OK}} = -175.0 \text{ m}E_{\text{h}}$, which is almost identical to the experimental value quoted in earlier papers (e.g. $E_{\text{coh}}^{\text{OK}} = -176 \text{ m}E_{\text{h}}$ in ref. 12). Our calculated value $E_{\text{coh}}^{\text{OK}} = -176.0 \text{ m}E_{\text{h}}$ thus agrees with the experimental value to within $\sim 1 \text{ m}E_{\text{h}}$ per formula unit.

These results for LiH show the possibility of extracting accurate values for the properties of bulk crystals from quantum chemistry calculations on free clusters. It is likely that the use of clusters embedded in suitably designed arrays of point charges would be still more efficient. Although LiH is clearly a favourable case, trial calculations on LiF and MgO suggest that the strategy will work well for other ionic materials. The performance of the method on other types of solid is as yet un-tested, but we are optimistic that the approach will be transferable, owing to the generality of the short-range nature of the correlation phenomenon. The limiting processes we have described also allow the calculation of the formation energies of surfaces, edges and corners, as will be reported elsewhere. It is likely that periodic implementa-

tions of MP2 will soon become practical tools for studying bulk and surface properties; but our strategy should remain a valuable tool for the computation of corrections to higher levels of theory. These corrections work especially well in the current framework, and offer the possibility of extending the whole range of successful tools from molecular electronic structure theory to the solid state.

The authors are grateful to Prof. Neil Allan for helpful discussions, and FRM gratefully acknowledges funding from The Royal Society. The work of DA was conducted as part of a EURYI scheme award.

References

- 1 G. Stollhoff and P. Fulde, *Z. Phys. B*, 1977, **26**, 251.
- 2 P. Y. Ayala, K. N. Kudin and G. E. Scuseria, *J. Chem. Phys.*, 2001, **115**, 9698.
- 3 (a) H. Stoll, *Phys. Rev. B*, 1992, **46**, 6700; (b) H. Stoll, *Chem. Phys. Lett.*, 1992, **191**, 548; (c) H. Stoll, *J. Chem. Phys.*, 1992, **97**, 8449.
- 4 (a) P. Pulay, *Chem. Phys. Lett.*, 1983, **100**, 151; (b) S. Saebo and P. Pulay, *Chem. Phys. Lett.*, 1985, **113**, 13.
- 5 C. Pisani, M. Busso, G. Capecchi, S. Casassa, R. Dovesi, L. Maschio, C. Zicovich-Wilson and M. Schütz, *J. Chem. Phys.*, 2005, **122**, 094113.
- 6 B. Paulus, *Phys. Rep.*, 2006, **428**, 1.
- 7 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. Dobbyn, 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>.
- 8 (a) F. Weigend, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4285; (b) F. Weigend, F. M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143.
- 9 R. Dovesi, C. Ermondi, E. Ferrero, C. Pisani and C. Roetti, *Phys. Rev. B*, 1984, **29**, 3591.
- 10 (a) S. Baroni, S. de Gironcoli, A. Dal Corso and P. Giannozzi, *Rev. Mod. Phys.*, 2001, **73**, 515; (b) G. Kresse, J. Furthmüller and J. Hafner, *Europhys. Lett.*, 1995, **32**, 729.
- 11 (a) G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169; (b) S. Scandolo, P. Giannozzi, C. Cavazzoni, S. de Gironcoli, A. Pasquarello and S. Baroni, *Z. Kristallogr.*, 2005, **220**, 574.
- 12 A. Shukla, M. Dolg, P. Fulde and H. Stoll, *Phys. Rev. B*, 1999, **60**, 5211.
- 13 *J. Phys. Chem. Ref. Data*, ed. M. W. Chase, NIST-JANAF Thermochemical Tables, 4th edn, American Institute of Physics, 1998.