

**Calculation of properties of crystalline lithium hydride using correlated wave function theory**S. J. Nolan,<sup>1</sup> M. J. Gillan,<sup>2,3</sup> D. Alfè,<sup>2,3,4</sup> N. L. Allan,<sup>1</sup> and F. R. Manby<sup>1</sup><sup>1</sup>*Centre for Computational Chemistry, School of Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom*<sup>2</sup>*London Centre for Nanotechnology, UCL, London WC1H 0AH, United Kingdom*<sup>3</sup>*Department of Physics and Astronomy, UCL, London WC1E 6BT, United Kingdom*<sup>4</sup>*Department of Earth Sciences, UCL, London WC1E 6BT, United Kingdom*

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The lattice parameter, bulk modulus, and cohesive energy of lithium hydride are calculated to very high accuracy through a combination of periodic and finite-cluster electronic structure calculations. The Hartree-Fock contributions are taken from earlier work in which plane-wave calculations were corrected for pseudopotential errors. Molecular electronic structure calculations on finite clusters are then used to compute the correlation contributions and finite-size effects are removed through the hierarchical scheme. The systematic improvability of the molecular electronic structure methods makes it possible to converge the static cohesive energy to within a few tenths of a millihartree. Zero-point energy contributions are determined from density functional theory phonon frequencies. All calculated properties of lithium hydride and deuteride agree with empirical observations to within experimental uncertainty.

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**I. INTRODUCTION**

Computational studies of crystalline solids are dominated by density functional theory (DFT; see, for example, Ref. 1), but despite many successes, DFT does have some drawbacks. In conventional formulations, there is no description of long-range dispersion; accuracy has been found inadequate for the description of processes at surfaces (see, for example, Ref. 2); and, worst of all, there is no clear route for systematic improvement of DFT results. Quantum Monte Carlo<sup>3</sup> is widely used for solids, and is in principle exact. But the fixed-node approximation and pseudopotential errors prevent systematic improvement beyond a certain point, and geometry optimization, though possible, is not straightforward.

Wave-function-based methods for molecular electronic structure theory, such as Møller-Plesset (MP) and coupled-cluster (CC) theory, are systematically improvable: generally it is clear how a calculation can be improved toward the exact nonrelativistic, Born-Oppenheimer solution. Further corrections for these smaller effects can be added, and very high accuracy can be achieved for thermochemistry,<sup>4,5</sup> spectroscopy,<sup>6</sup> and kinetics.<sup>7</sup>

Various approaches have been adopted to apply these molecular methods to solids. The most obvious (but least straightforward) is to implement periodic methods directly. This has been achieved for MP2 theory in at least three different ways: Ayala *et al.* reported an atomic-orbital-driven Laplace-transform MP2 method,<sup>8</sup> the CRYSCOR code uses a combination of local correlation methods and Poisson density fitting,<sup>9,10</sup> and MP2 is now implemented in VASP using plane waves.<sup>11</sup>

Simpler methods can be formulated by attempting to learn about the bulk material from calculations on smaller fragments. In the incremental scheme<sup>12–14</sup> a many-body expansion of the correlation energy is combined with periodic Hartree-Fock (HF) calculations to estimate properties of the crystal. In this paper, we will use the hierarchical

method,<sup>15,16</sup> by which the electron correlation energy of the solid can be determined to high accuracy from calculations on finite clusters through careful subtraction of edge effects.

In our earlier work, we introduced the hierarchical method and made a preliminary calculation on lithium hydride at one value of the lattice parameter. The aim of the present paper is to set out a calculation of the lattice parameter, bulk modulus, and cohesive energy of crystalline lithium hydride to the highest accuracy currently feasible. This serves two important purposes: first we establish (by comparison with experiment) the very high accuracy that can be achieved by the hierarchical method; second, we offer a number of benchmarks that can aid in the development and calibration of other periodic electronic structure codes.

**II. HIERARCHICAL METHOD**

The hierarchical method has been described before,<sup>15</sup> so here only the salient features will be reported, for the specific case of an ionic solid MX in the rock-salt structure. All energies are calculated per formula unit and relative to the free atoms. The static cohesive energy can be decomposed into Hartree-Fock and correlation contributions

$$E_{\text{coh}} = E_{\text{coh}}^{\text{HF}} + E_{\text{coh}}^{\text{cor}}. \quad (1)$$

The correlation contribution  $E_{\text{coh}}^{\text{cor}}$  is dominated by a term  $E_{\text{mol}}^{\text{cor}}$  that describes the correlation contribution to the energy required to break a single MX molecule into its constituent atoms. A correction, called the correlation residual  $\Delta E_{\text{coh}}^{\text{cor}}$ , is then needed to account for the correlation contribution to the energy required to split the crystal into separated MX molecules. Here, “molecule” refers to the MX unit with its crystalline interatomic separation.

Thus, the strategy for computing the static cohesive energy is to evaluate

$$E_{\text{coh}} = E_{\text{coh}}^{\text{HF}} + E_{\text{mol}}^{\text{cor}} + \Delta E_{\text{coh}}^{\text{cor}} \quad (2)$$

using periodic Hartree-Fock theory for the first term, and accurate molecular electronic structure theory for the second. The final term is estimated through calculations on finite clusters. For the case of LiH, the first term has recently been determined to high accuracy,<sup>17</sup> and the second, for such a small system, can easily be computed to extremely high accuracy. It will be shown here that for this system, the correlation residual can also be computed to high accuracy, leading to computed properties for this material of unsurpassed reliability.

To proceed, we define an analogous correlation residual for a finite cluster of size  $l \times m \times n$

$$\Delta E_{lmn}^{\text{cor}} = E_{lmn}^{\text{cor}} - \frac{lmn}{2} E_{112}^{\text{cor}} \quad (3)$$

where  $E_{lmn}^{\text{cor}}$  is the correlation energy of the corresponding block, and  $E_{112}^{\text{cor}}$  is simply the special case of this quantity for a single MX unit. Clearly atoms at the surfaces of the cluster will not be representative of the bulk crystal. In fact there are four distinct environments for the atoms in cuboidal clusters: corners, edges, faces and bulk. Each of these contributes differently to the correlation residual, and in particular we can write

$$\begin{aligned} \Delta E_{lmn}^{\text{cor}} = & 8E^{000} + 4[(l-2) + (m-2) + (n-2)]E^{001} + 2[(l-2) \\ & \times (m-2) + (l-2)(n-2) + (m-2)(n-2)]E^{011} \\ & + (l-2)(m-2)(n-2)E^{111}, \end{aligned} \quad (4)$$

when  $l, m, n > 2$ . Here,  $E^{000}$ ,  $E^{001}$ ,  $E^{011}$ , and  $E^{111}$  are the contributions to the correlation residual from atoms at the corners, edges, faces and in the bulk. A similar (and formally equivalent) formula was derived in our earlier work based on considering the extensivity of the energy with respect to extensions in any of the three Cartesian directions.<sup>15</sup>

For a given maximum number of atoms, a set of four distinct clusters is chosen and Eq. (4) is solved as a set of simultaneous equations. The clusters are chosen according to the algorithm in Ref. 15, ensuring that the most bulklike clusters are included. The bulk correlation residual can then be obtained as  $\Delta E_{\text{coh}}^{\text{cor}} = 2E^{111}$ .

### III. BULK PROPERTIES OF LITHIUM HYDRIDE

The Hartree-Fock contribution to the cohesive energy  $E_{\text{coh}}^{\text{HF}}$  is known to high precision at a range of lattice parameters.<sup>17</sup> The remaining task is to evaluate the correlation contributions  $E_{\text{mol}}^{\text{cor}}$  and  $\Delta E_{\text{coh}}^{\text{cor}}$ , and convergence of these quantities to high accuracy was initially studied at the experimental room-temperature lattice parameter,  $a=4.084$  Å. All of the molecular electronic structure calculations were performed using the MOLPRO package, unless otherwise noted.<sup>18</sup>

LiH has only four electrons, so the molecular-correlation contribution  $E_{\text{mol}}^{\text{cor}}$  can be found to exceptionally high accuracy. For this term, all-electron full configuration interaction (ae-FCI) is used with a basis-set correction computed at the level of all-electron coupled-cluster theory with full treatment of single and double excitations and perturbative treat-

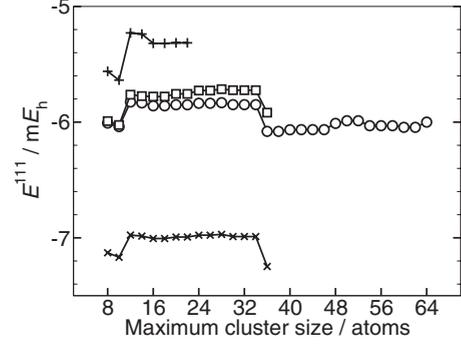


FIG. 1. Coefficients  $E^{111}$  for LiH with lattice-parameter  $a = 4.084$  Å using CCSD(t)/cc-pVTZ (pluses), MP2/cc-pVQZ (squares), MP2/cc-pVTZ (circles) and ae-MP2/cc-pCVTZ (crosses).

ment of triple excitations [ae-CCSD(T)]. The binding energy computed using ae-FCI/cc-pCVTZ exceeds that given by ae-CCSD(T)/cc-pCVTZ by only  $15 \mu E_h$ . The basis-set limit was approached using ae-CCSD(T)/cc-pCV[TQ]Z, where the notation cc-pCV[TQ]Z implies that the correlation energies from calculations in the cc-pCVTZ and cc-pCVQZ basis sets were extrapolated using the  $L^{-3}$  scheme and added to the cc-pCVQZ Hartree-Fock energy.<sup>19</sup>

Counterpoise corrections for basis-set-superposition error were tested, and were found to be completely negligible, for example, just  $3 \mu E_h$  for cc-pCVQZ. The Hartree-Fock diagonal Born-Oppenheimer correction,<sup>20</sup>  $\langle \Psi | \hat{T}_{\text{nuc}} | \Psi \rangle$ , was calculated using with the PSI3 electronic structure package,<sup>21</sup> and the minute destabilizing effect ( $7 \mu E_h$ ) was considered negligible. Relativistic corrections were also found to be completely negligible, as expected for such light elements.

We compute the correlation residual through MP2/cc-pVTZ calculations up to large cluster sizes ( $N=64$ ) with higher-level corrections calculated up to smaller maximum cluster sizes. The rationale for this approximation is that the corrections to the correlation residual converge much more rapidly with respect to  $N$  than do the individual energies. Density fitting was used for the frozen-core MP2/cc-pVTZ calculations (which involved calculations up to 64 ions) and for the basis-set corrections. In these cases, Hartree-Fock theory was performed using the DF-HF method<sup>22</sup> with the cc-pVnZ/JKFIT basis on hydrogen, and the nZVPP/JKFIT basis on Li.<sup>23</sup> The density-fitted MP2 (DF-MP2) calculations used the corresponding cc-pVnZ/MP2FIT basis sets of Weigend *et al.*<sup>24</sup> and Hättig.<sup>25</sup> For MP2/cc-pVTZ the error introduced to the  $N=16$  correlation residual by density fitting in both the HF and MP2 calculation is only around  $10 \mu E_h$ .

The  $E^{111}$  coefficients obtained are plotted in Fig. 1 for MP2/cc-pVTZ, CCSD(T)/cc-pVTZ, MP2/cc-pVQZ, and ae-MP2/cc-pCVTZ. The small jumps in each line have been explained previously in terms of the structural characteristics of the clusters involved;<sup>15</sup> but here it is worth noting that the lines for different methods are closely parallel, justifying the use of smaller  $N$  for high-level corrections. In common with many computational studies, we rely on the additivity of corrections from higher-level methods. Such approaches are well-tested and well-documented in the literature (represent-

TABLE I. Analysis of additivity errors for the correlation contributions to the binding energy of two clusters per formula unit relative to isolated LiH molecule. All errors are in microhartree. CC is used as an abbreviation for CCSD(T); and (C)VnZ for cc-p(C)VnZ. The first three rows test the error in using an MP2 basis-set correction; MP2 for the core-correlation correction; smaller basis sets for the core correction. The final row contains the discrepancy between the ae-CCSD(T)/CVQZ energies and energies estimated by MP2/VTZ together with all corrections.

	$1 \times 2 \times 2$	$2 \times 2 \times 2$
$E_{\text{VQZ}}^{\text{CC}} - [E_{\text{VTZ}}^{\text{CC}} + E_{\text{VQZ}}^{\text{MP2}} - E_{\text{VTZ}}^{\text{MP2}}]$	58	93
$E_{\text{CVTZ}}^{\text{ae-CC}} - [E_{\text{VTZ}}^{\text{CC}} + E_{\text{CVTZ}}^{\text{ae-MP2}} - E_{\text{VTZ}}^{\text{MP2}}]$	1	-22
$E_{\text{CVQZ}}^{\text{ae-MP2}} - [E_{\text{VQZ}}^{\text{MP2}} + E_{\text{CVTZ}}^{\text{ae-MP2}} - E_{\text{VTZ}}^{\text{MP2}}]$	-101	-126
$E_{\text{CVQZ}}^{\text{ae-CC}} - [E_{\text{VTZ}}^{\text{MP2}} + \text{all corrections}]$	-44	-66

tative examples can be found in Refs. 4, 26, and 27) but nevertheless for high-accuracy work it is always worth calibrating the error that arises from nonadditivity. To this end, we calculated correlation contributions to the binding energies of the  $1 \times 2 \times 2$  and  $2 \times 2 \times 2$  clusters (per formula unit and relative to isolated molecules) at a variety of levels of theory. We then analyzed the additivity error that arises from treating (i) basis-set corrections using MP2 instead of coupled-cluster theory; (ii) core-correlation corrections using MP2; and (iii) core-correlation corrections using smaller basis sets. The results are presented in Table I, and indicate that errors are typically on the order of  $100 \mu E_h$ .

Here, we further analyze the convergence of the hierarchical procedure, by evaluating several different  $E^{111}$  contributions for each maximum cluster size  $N$ . For a given value of  $N$  we form a lexicographically ordered list of clusters, as before. We then select all quadruples of clusters not larger than  $N$  and not smaller than the smallest cluster in the standard hierarchical method for  $N-2$ . This provides a number of different estimates for the MP2/cc-pVTZ  $E^{111}$  for each cluster size, and the average of these data is compared with the standard hierarchical result in Fig. 2. Qualitatively the performance of the two approaches is equivalent: there are oscillations of the same magnitude where the calculations no

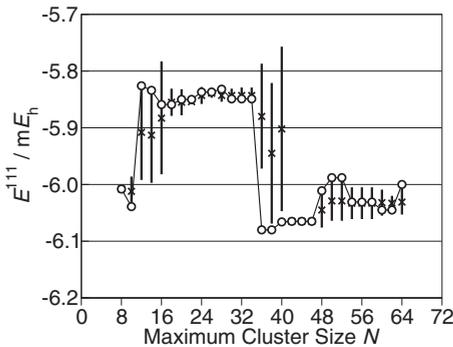


FIG. 2. Coefficients  $E^{111}$  for LiH with lattice-parameter  $a = 4.084 \text{ \AA}$  using MP2/cc-pVTZ in the hierarchical scheme (circles) and by averaging energies obtained with all possible quadruples of clusters at size  $N$  (crosses; see text for exact specification). Standard deviation is denoted by the vertical bars.

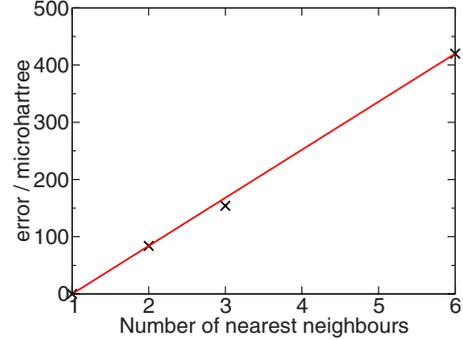


FIG. 3. (Color online) Error in CCSD(T) [defined as  $\text{CCSDT(Q)} - \text{CCSD(T)}$ ] as a function of number of nearest neighbors. The crosses arise from clusters  $1 \times 1 \times 2$ ,  $1 \times 2 \times 2$ ,  $2 \times 2 \times 2$ , and from the bulk cohesive energy (computed in the hierarchical method with  $N=8$ ). The first datum has an error of zero by definition, since these are errors in binding energies relative to the LiH molecule. The straight line is that which passes through the first two points.

longer rely on chains and sheets. For values of  $N$  large enough that no information is derived from sheets, the average energy becomes almost constant, with a standard deviation of around  $20-30 \mu E_h$ .

For our reference lattice parameter ( $a = 4.084 \text{ \AA}$ ) we have performed higher-level calculations to assess convergence. In particular we performed the first step of hierarchical analysis (with  $N=8$ ) using  $\text{CCSDT/cc-pVDZ}$  and  $\text{CCSDT(Q)/cc-pVDZ}$  with the MRCC code of Kállay.<sup>28,29</sup> The contribution to the cohesive energy of the crystal is almost half a millihartree, so for more complicated solids it is very likely that effects beyond CCSD(T) will be needed to achieve chemical accuracy.

It is perhaps surprising that CCSD(T) is in error by this amount: often (T) overestimates the triples effect, and therefore to some extent compensates for the lack of quadruples; here we find that the discrepancy between CCSD(T) and CCSDT(Q) is typically 10–20 times greater than the discrepancy between CCSDT and CCSDT(Q). The beyond-(T) correction to the cohesive energy arises entirely from breaking the crystal into LiH molecules (since LiH itself has only two valence electrons all of these methods are identical to CCSD).

To investigate this further we computed binding energies using CCSD(T), CCSDT and CCSDT(Q) per formula unit and relative to free LiH molecules. For the cluster size  $1 \times 2 \times 2$ , CCSD(T) and CCSDT differ from CCSDT(Q) by  $-84 \mu E_h$  and  $-4 \mu E_h$ , respectively. For  $2 \times 2 \times 2$ , the discrepancies rise to  $-154 \mu E_h$  and  $-12 \mu E_h$ , respectively, and the figures of  $-420 \mu E_h$  and  $-50 \mu E_h$  for the CCSDT and CCSDT(Q) contributions to the bulk cohesive energy seem to fall reasonably in line with a pattern of increasing contributions with increasing numbers of neighbors: see Fig. 3. The straight line in the plot is that implied by the first two points, suggesting that it might be possible to approximate the beyond-(T) corrections to the cohesive energy using calculations on just four ions. To test the additivity of basis-set and correlation-level corrections, we computed the binding energy of the  $1 \times 2 \times 2$  cluster using CCSD(T)/cc-pVTZ and

CCSDT/cc-pVTZ, and encouragingly obtained almost exactly the same value for the beyond-(T) contribution:  $-84 \mu E_h$ .

At this geometry we verified that other effects are small. We computed the effect of the diagonal Born-Oppenheimer correction on  $E^{111}$  using HF/cc-pVTZ with  $N=8$ , with the PSI3 package.<sup>21</sup> For such light elements relativistic effects are expected to be extremely small, and Douglas-Kroll HF/cc-pVDZ (Refs. 30–32) calculations (with  $N=8$ ) indicate an effect of the order  $10 \mu E_h$ . Relativity was therefore neglected.

In order to compare with experiment, the contribution of zero-point energy and its variation with lattice parameter must be considered. This is obtained from periodic DFT calculations. For semi-ionic materials like LiH computed phonon frequencies are generally correct to better than 5%.<sup>33</sup> We calculated phonon dispersion relations by the linear-response and small displacement methods,<sup>34,35</sup> using the VASP (Ref. 36) and ESPRESSO (Ref. 37) codes. As noted previously,<sup>15</sup> the results in the local-density and generalized-gradient approximations at the reference lattice parameter differ by just  $0.2 mE_h$ .

This concludes the evaluation of all contributions to the cohesive energy at the reference lattice parameter of  $4.084 \text{ \AA}$ . The results of all of these calculations are summarized in Table II, and lead to a total cohesive energy (at this unrelaxed lattice parameter) of  $-175.3 mE_h$ .

At is this stage it is perhaps worth reviewing the computational cost of each correlation correction. The computational scaling with respect to system size of MP2, CCSD(T), CCSDT, and CCSDT(Q) is  $\mathcal{O}(N^5)$ ,  $\mathcal{O}(N^7)$ ,  $\mathcal{O}(N^8)$ , and  $\mathcal{O}(N^9)$ , respectively. The scaling with respect to number of basis functions (for fixed molecular size) is at least  $m^4$ . On a single Opteron processor (2 GHz) the largest MP2 calculation (64 ions,  $4 \times 4 \times 4$ , cc-pVTZ) took just over 7 h. It should be noted, though, that modern implementations of MP2 use screening (and in this case also density fitting) so effectively that most of this time is spent doing the preliminary Hartree-Fock calculation. The largest CCSD(T) (16 ions,  $2 \times 2 \times 4$ , cc-pVTZ) took around 4 h, but in this size regime, the preceding Hartree-Fock calculation only consumes a small fraction of the time. The implementation of higher-order corrections is extremely complicated, and in fact the most expensive calculations of all were the CCSDT(Q) corrections on 8-ion systems. The very high scaling of this method is such that it would be difficult to apply it to more complicated solids; but in any case the correction from connected quadruples is reassuringly small.

We next repeated the calculation of all of the main contributions to the cohesive energy at several different values of the lattice parameter. Most of the variation in the energy resides in the Hartree-Fock and molecular-correlation contributions, and these were evaluated on a grid of seven values at intervals of  $0.1 \text{ \AA}$ . Smaller contributions (and more importantly, contributions whose variation with lattice parameter is essentially linear) were computed at four points with intervals of  $0.2 \text{ \AA}$ . The contributions to the correlation residual are shown in Table III. Note that the minute but very expensive CCSDT(Q) corrections were not computed at multiple lattice-parameter values.

The Hartree-Fock,<sup>17</sup> molecular-correlation and residual contributions are given in Table IV together with zero-point

TABLE II. Contributions to the cohesive energy of LiH calculated using the hierarchical method at a fixed lattice parameter of  $4.084 \text{ \AA}$ . The abbreviation  $VnZ$  is used for cc-pVnZ; V[TQ]Z indicates that cc-pVTZ and cc-pVQZ correlation energies have been cubically extrapolated.

Contribution	Energy/ $mE_h$	Comments
Hartree-Fock	-131.90	PWSCF+ pseudopotential corrections
Corr. (mol.) <sup>a</sup>	-38.40	CCSD(T)/CV[TQ]Z+ $\delta$ FCI/CVTZ
MP2	-12.00	MP2/VTZ $N=64$
Core corr. <sup>b</sup>	-2.29	ae-MP2/CVTZ $N=16$
Basis <sup>c</sup>	+0.80	V[TQ]Z $N=36$ and V[Q5]Z $N=12$
$\delta$ CCSD(T) <sup>d</sup>	+1.08	CCSD(T)/VTZ $N=16$
$\delta$ CCSDT <sup>e</sup>	-0.42	CCSDT/VDZ $N=8$
$\delta$ CCSDT(Q) <sup>f</sup>	-0.05	CCSDT(Q)/VDZ $N=8$
DOBC <sup>g</sup>	+0.06	HF/VTZ $N=8$
Zero point	+7.79	from GGA phonon frequencies
Total	-175.31	

<sup>a</sup>Molecular contribution to the cohesive energy, computed as described in the text.

<sup>b</sup>Correction for core correlation, computed as ae-MP2/CVTZ—MP2/VTZ with  $N=16$ .

<sup>c</sup>Basis-set incompleteness correction, computed as MP2/V[TQ]Z—MP2/VTZ with  $N=36$  plus MP2/V[Q5]Z—MP2/V[TQ]Z with  $N=12$ .

<sup>d</sup>Main coupled-cluster correction: computed as CCSD(T)/VTZ—MP2/VTZ with  $N=16$ .

<sup>e</sup>Correction for full triples computed as CCSDT/VDZ—CCSD(T)/VDZ with  $N=8$ .

<sup>f</sup>Correction for full perturbative quadruples computed as CCSDT(Q)/VDZ—CCSDT/VDZ with  $N=8$ .

<sup>g</sup>Diagonal Born-Oppenheimer correction.

contributions for  $^7\text{LiH}$  and  $^7\text{LiD}$ . The lattice parameter, bulk modulus, and cohesive energy of these isotopomers were determined from the tabulated energy data by two methods. First the finely tabulated energies  $E_{\text{coh}}^{\text{HF}} + E_{\text{mol}}^{\text{cor}}$  (Table IV) were fitted to a sixth-order polynomial. The corrections  $\Delta E_{\text{coh}}^{\text{cor}} + E_{\text{ZP}}$  were then fitted to a cubic polynomial, and the sum of these two polynomials was minimized to obtain the opti-

TABLE III. Contributions to the correlation residual of the crystal at various lattice parameters. All energies in millihartree, and the details of each term are exactly as described in Table II unless otherwise noted.

$a/\text{\AA}$	MP2/VTZ	Core	Basis <sup>a</sup>	$\delta$ CCSD(T)	$\delta$ CCSDT
3.684	-15.094	-3.534	+0.104	+0.830	-0.365
3.884	-13.474	-2.850	+0.197	+0.928	-0.391
4.084	-11.998	-2.294	+0.294	+1.080	-0.418
4.284	-10.620	-1.842	+0.401	+1.282	-0.444

<sup>a</sup>Basis-set correction using MP2/V[TQ]Z—MP2/VTZ with  $N=16$ . Note that these corrections differ significantly from the more thorough correction shown in Table II, but we found the variation of the additional basis-set effects with respect to lattice parameter to be extremely small.

TABLE IV. Energy contributions in millihartree to the cohesive energy of the crystal at various lattice parameters. The correlation residual  $\Delta E_{\text{coh}}^{\text{cor}}$  is the sum of the energy columns of Table III.

$a/\text{\AA}$	$E_{\text{coh}}^{\text{HF}}$	$E_{\text{mol}}^{\text{cor}}$ <sup>a</sup>	$\Delta E_{\text{coh}}^{\text{cor}}$	$E_{\text{ZP}}(\text{LiH})$	$E_{\text{ZP}}(\text{LiD})$
3.684	-124.135	-37.909	-18.059	10.530	8.330
3.784	-127.634	-37.980			
3.884	-129.986	-38.080	-15.590	9.040	7.140
3.984	-131.365	-38.211			
4.084	-131.910	-38.371	-13.336	7.790	6.120
4.184	-131.747	-38.559			
4.284	-130.978	-38.773	-11.223	6.630	5.200

<sup>a</sup>Computed as ae-FCI/cc-pCVTZ plus a basis-correction using ae-CCSD(T)/cc-pCV[TQ]Z.

mized lattice parameter. The cohesive energy was further refined by the addition of small corrections from Table II. As an independent check, the energies at the four points for which all energy contributions were computed were fitted to the Birch-Murnaghan<sup>38,39</sup> equation of state. This yielded lattice parameters, bulk moduli, and cohesive energies that agreed with those obtained from polynomial interpolation to within 0.0002  $\text{\AA}$ , 0.05 GPa, and 1  $\mu E_{\text{h}}$ , respectively.

Since considerable effort has been made on the accuracy of the theoretical treatment of lithium hydride, it is worth briefly reviewing the most reliable experimental data. The cohesive energy of the hydride can be computed from standard thermochemical quantities, as shown in Table V. Two different cycles are possible: relying in case (i) on tabulated zero-temperature heats of formation of  $\text{H}_{(\text{g})}$ ,  $\text{Li}_{(\text{g})}$  and  $\text{LiH}_{(\text{s})}$ ; and in case (ii) on tabulated room-temperature heats of formation coupled with low-temperature heat-capacity data. The two values disagree by around 1.5  $\text{kJ mol}^{-1}$  giving some indication of the maximum reliability of the experimentally determined cohesive energy. For the deuteride only route (ii) was possible, as shown in Table V.

TABLE V. Derivation of zero-temperature cohesive energies of LiX (X=H or D) from thermochemical data. All data are taken from the JANAF tables (Ref. 40) unless otherwise noted; and all energies are given in  $\text{kJ/mol}$ . The available data allow two thermodynamic cycles for the  ${}^7\text{LiH}$  isotopomer, and one for  ${}^7\text{LiD}$ .

	LiH		LiD
	$T=0\text{ K}$	$T=298\text{ K}$	$T=298\text{ K}$
$-\Delta_f H(\text{X}_{(\text{g})}, 0\text{ K})$	-216.035	-216.035	-219.807
$-\Delta_f H(\text{Li}_{(\text{g})}, T)$	-157.725	-159.300	-159.300
$\Delta_f H(\text{LiX}_{(\text{s})}, T)$	-85.548	-90.625	-91.144 <sup>a</sup>
$H_{298}(\text{Li}_{(\text{g})}) - H_0(\text{Li}_{(\text{g})})$		4.622	4.622
$[H_{298}(\text{X}_{2(\text{g})}) - H_0(\text{X}_{2(\text{g})})]/2$		4.234	4.285
$H_0(\text{LiX}_{(\text{s})}) - H_{298}(\text{LiX}_{(\text{s})})$		-3.778	-4.596 <sup>b</sup>
$E_{\text{coh}}$	-459.308	-460.882	-465.940

<sup>a</sup>Taken from Gunn and Green (Ref. 41).

<sup>b</sup>Computed by integration by of heat-capacity data from Yates *et al.* (Ref. 42).

TABLE VI. Theoretical values for the zero-temperature lattice parameter, bulk-modulus, and cohesive energy of LiH and LiD (per formula unit and relative to free atoms). Experimental values are shown for comparison.

		$a_0/\text{\AA}$	$B_0/\text{GPa}$	$E_{\text{coh}}/mE_{\text{h}}$
${}^7\text{LiH}$	This work	4.062	33.2	-175.3
	Experiment	4.061(1) <sup>a</sup>	33–38 <sup>b</sup>	-175.6, -174.9 <sup>c</sup>
${}^7\text{LiD}$	This work	4.046	34.2	-177.0
	Experiment	4.045(1) <sup>a</sup>	33.5(4) <sup>d</sup>	-177.5 <sup>c</sup>

<sup>a</sup>Neutron scattering,  $T=93\text{ K}$  for LiH and  $T=83\text{ K}$  for LiD (Ref. 43); the lattice parameter at 0 K would probably not differ to within the experimental uncertainty. See text for details.

<sup>b</sup>These 0 K numbers were obtained from various experimental results at 300 K by scaling by 1.06 (Ref. 44); see Ref. 14 and references therein.

<sup>c</sup>Computed from the thermodynamic cycles given in Table V.

<sup>d</sup>Measured by neutron diffraction at 300 K (Ref. 45) and corrected to 0 K by multiplication by 1.06 (Ref. 44). The errors associated with the scaling procedure are expected to be much smaller than the quoted experimental uncertainty (Ref. 44).

The theoretical results for both, isotopomers are compared to experimental values in Table VI. In all cases, excellent agreement with experiment is found. The cohesive energy for LiH falls about halfway between the two experimentally determined values, and for LiD the discrepancy between experiment and theory is one half of a millihartree. The lattice parameters have been measured by neutron diffraction at 93 K (for LiH) and 83 K (for LiD).<sup>43</sup> An earlier x-ray diffraction study, although less reliable owing to contamination by Li metal, revealed that the contraction on cooling from 80 to 12.1 K amounted to no more than 0.001  $\text{\AA}$ , and comparable to the quoted uncertainty in both experiments. Values for the bulk modulus vary quite widely between different experiments, but are in broad agreement with the theoretically determined values.

#### IV. BENCHMARK RESULTS

Having established the accuracy of our overall procedure through careful comparison with experiment, it seems reasonable to take the simple additional steps to provide benchmark data against which other periodic electronic structure methods can be tested. In Table VII, we provide our basis-set-limit estimates of the static cohesive energy of LiH using Hartree-Fock, MP2, and coupled-cluster theory, and compare with other calculations performed using the newly developed plane-wave MP2 code in VASP.<sup>11</sup> Also included in the table is the highly converged Hartree-Fock result of Paier *et al.* using the CP2K and GAUSSIAN codes.<sup>46</sup> These are the best converged values (at their respective levels of theory) available in the literature, but there have been numerous earlier calculations.

An early study with the CRYSTAL code gave the Hartree-Fock static cohesive energy as  $-130\text{ m}E_{\text{h}}$  (at  $a=4.102\text{ \AA}$ ) by Dovesi *et al.*,<sup>47</sup> it was later determined as  $-131\text{ m}E_{\text{h}}$  (at  $a=4.112\text{ \AA}$ ) by Bellaïche and Lévy,<sup>48</sup> and as  $-129\text{ m}E_{\text{h}}$

TABLE VII. Our all-electron basis-set limit estimates of the static cohesive energy (millihartree) of lithium hydride at  $a = 4.084 \text{ \AA}$  at different levels of electron correlation, and comparison with other highly converged calculations computed by Marsman *et al.* using VASP; and by Paier *et al.* using CP2K and GAUSSIAN.

Method	This work	VASP	CP2K
HF	-131.90	-131.67	-131.95
MP2	-175.33	-175.66	
CCSD	-180.75		
CCSD(T)	-182.65		
CCSDT	-183.08		
CCSDT(Q)	-183.13		

(at  $a = 4.106 \text{ \AA}$ ) by Shukla *et al.*<sup>14</sup> The last authors also produced correlated values for the cohesive energy ( $-164 \text{ mE}_h$ ) and lattice parameter ( $a = 4.106 \text{ \AA}$ ) through the incremental scheme. The large discrepancy between this value and the static cohesive energy (of about  $-183 \text{ mE}_h$ ) produced here arises from a variety of approximations made in the earlier work; but it is highly likely that the difference mostly arises from their use of extremely limited one-particle basis sets (with  $3s1p$  on H and  $2s1p$  on Li) in the correlation treatment.

## V. CONCLUSIONS

Using the hierarchical scheme it is possible to obtain highly converged properties of a simple ionic solid like lithium hydride. Edge effects dominate properties of the small clusters that are used, but in the hierarchical scheme these effects are carefully subtracted to reveal information about the bulk crystal. An alternative perspective on the suc-

cess of the method is provided by Nolan *et al.*<sup>16</sup>

Through use of the extensively tested hierarchies of molecular electronic structure theory, corrections can be made for higher-order correlation effects, correlation of the core electrons and basis-set effects. In all cases, the error introduced by the simple additive scheme for combining these corrections has been assessed and found to be small. Considering the various sources of error in these calculations (non-additivity, residual correlation, and basis-set effects, incomplete convergence of the hierarchical scheme, and use of DFT zero-point corrections) it would seem that the computed cohesive energy is accurate to within a few tenths of a millihartree. While all of these approximations could be refined, a significant reduction in the errors below this level would at least involve CCSD(T) calculations in larger basis sets and on larger clusters, incurring an enormous increase in computational cost.

As a by-product of the study we have established benchmark results for a variety of methods, so that as periodic MP2 and even coupled-cluster codes become available they can be tested against this simple test system. Moreover, an independent check of our methodology is provided through excellent agreement (to within a few tenths of a millihartree) with the MP2 cohesive energy computed using entirely different techniques.<sup>11</sup>

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