

High-Precision Calculation of Hartree-Fock Energy of Crystals

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Received 24 January 2008; Accepted 16 April 2008

DOI 10.1002/jcc.21033

Published online 5 June 2008 in Wiley InterScience (www.interscience.wiley.com).

Abstract: When using quantum chemistry techniques to calculate the energetics of bulk crystals, there is a need to calculate the Hartree-Fock (HF) energy of the crystal at the basis-set limit. We describe a strategy for achieving this, which exploits the fact that the HF energy of crystals can now be calculated using pseudopotentials and plane-wave basis sets, an approach that permits basis-set convergence to arbitrary precision. The errors due to the use of pseudopotentials are then computed from the difference of all-electron and pseudopotential total energies of atomic clusters, extrapolated to the bulk-crystal limit. The strategy is tested for the case of the LiH crystal, and it is shown that the HF cohesive energy can be converged with respect to all technical parameters to a precision approaching $0.1 \text{ m}E_{\text{h}}$ per atom. This cohesive energy and the resulting HF value of the equilibrium lattice parameter are compared with literature values obtained using Gaussian basis sets.

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Key words: Hartree-Fock; crystal; solid; high accuracy; plane wave; pseudopotential

Introduction

Density functional theory (DFT) has dominated computational condensed-matter science for many years.¹ The reasons are well known: its mild scaling with number of atoms makes it possible to treat large complex systems; it allows basis-set convergence to be achieved to any desired tolerance; and atomic forces can be calculated at almost no extra cost, so that high-temperature dynamical and thermodynamic properties can be calculated by molecular dynamics simulation. However, the quantitative accuracy of DFT is often inadequate (see e.g. ref. 2), and there is currently no known way of systematically improving the description of electron correlation within DFT. These problems with DFT have stimulated efforts to apply wavefunction-based methods to condensed matter. These efforts date back many years, and include, for example, the incremental methods developed by Stoll, Fulde, and co-workers.^{3–7} In the incremental approach, the total energy is divided into Hartree-Fock and correlation parts, and the correlation energy is decomposed according to a many-body expansion into single-atom, atom-pair, atom-triplet, etc... terms. The approach has been successfully used to calculate the cohesive energy, equilibrium lattice parameter, and other properties of bulk crystals.⁷ Recently, there have also

been efforts to implement periodic versions of correlated quantum chemistry techniques.^{8–11}

We have recently reported¹² an alternative way of using wavefunction-based techniques to calculate the cohesive energy. This approach was designed particularly for ionic crystals such as LiH and MgO, though we believe it is more widely applicable. The total energy is separated, as usual, into Hartree-Fock and correlation energies, but the latter is then further separated into the correlation energy of the appropriate number of MX molecules (M = cation, X = anion), and the remainder, which we refer to as the “correlation residual”. This residual is then extracted by analysing its systematic variation over a large hierarchy of free or embedded clusters. (Details are given in our published paper.¹²) Taking LiH as an example, we showed that this approach is capable of giving the total cohesive energy within $\sim 1 \text{ m}E_{\text{h}}$ ($\sim 30 \text{ meV}$) per Li-H pair, and comparison with experiment confirmed this. However, it has become clear from our more recent work (unpublished) that in order to attain this level of precision, one of the major challenges is to calculate the

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Hartree-Fock energy sufficiently accurately. In particular, we have to ensure that errors of basis-set incompleteness in the Hartree-Fock energy of the crystal can be reduced to any desired tolerance. We note that the accurate calculation of the Hartree-Fock energy is also indispensable for achieving high accuracy by any other quantum chemistry method, for example the incremental method⁷ or periodic correlated methods.⁸ The purpose of this article is to outline the techniques we have developed to calculate the Hartree-Fock part of the cohesive energy of a crystal very accurately.

The most thoroughly tested way of calculating the Hartree-Fock energy of a periodic system is the CRYSTAL code,^{13–15} which employs Gaussian basis sets. (There is also an option for treating periodic systems in the GAUSSIAN code,¹⁶ which has been used recently for calculations on crystals.¹⁷) However, there seems to be a fundamental difficulty in achieving full basis-set convergence for condensed matter with Gaussian basis sets. The reason is that, as the size of the basis set is systematically increased, one always arrives at a point where near linear dependences between the basis functions render the calculations unstable. If the tolerance required for basis-set errors lies beyond this point, then the calculations simply cannot deliver what is required. (We remark also that it is difficult to demonstrate that convergence to a specified tolerance has been achieved, if one is incapable of achieving considerably better convergence.) This kind of difficulty means that basis-set convergence to better than ~ 1 mE_h/atom is generally difficult to attain for condensed matter with Gaussian basis sets, and for some systems the attainable accuracy may be worse than this.

The strategy we shall outline exploits the fact that the Hartree-Fock energy of crystals can now be calculated using plane-wave basis sets.^{18–21} There are two related ways of doing this. One way is to use conventional pseudopotential methods to eliminate the core electrons from the calculation and to represent the valence orbitals by pseudo-wavefunctions. The machinery to calculate the (pseudo-)Hartree-Fock energy in this way has been implemented in some of the standard codes, e.g. CASTEP¹⁹ and PWSCF.²² The other way is to use the PAW (projector augmented wave^{23,24}) implementation of Hartree-Fock described by Kresse et al.,¹⁸ which has been implemented in the VASP code.²⁵ With both these schemes, basis-set convergence to any specified tolerance is straightforward to obtain, simply by setting the plane-wave cut-off high enough. However, there is clearly a problem if we use a pseudopotential method: although we eliminate basis-set errors, we now incur another error due to the pseudopotential approximation, and this error must be corrected for.

The strategy we shall present is based on the conventional pseudopotential approach, and consists of two parts. In the first part, we calculate the (pseudo-)Hartree-Fock energy of the crystal in periodic boundary conditions with a plane-wave basis set, and we go to the required tolerance with respect to plane-wave cut-off and k -point sampling. To correct for the pseudopotential error, we then use exactly the same pseudopotential to calculate the Hartree-Fock energies of a large set of free clusters, using a standard quantum chemistry code. We then recalculate all the cluster formation energies using all-electron Hartree-Fock calculations. Finally, we perform a hierarchy analysis on the difference between the pseudo-HF and all-electron-HF cluster formation energies to extract the pseudopotential error in the bulk crystal. The technical details of these calculations will be explained in the following, and we shall

present practical calculations on the LiH crystal, to demonstrate that an accuracy of better than 1 mE_h/atom can indeed be obtained. LiH is a convenient choice, because it has the simple rock-salt structure, and because it has only a single valence electron per atom. The plane-wave calculations and the cluster calculations employed the PWSCF²² and MOLPRO²⁶ codes, respectively.

Throughout this article, “cohesive energy” means the Hartree-Fock energy per cation-anion pair of the perfect crystal minus the sum of the Hartree-Fock energies of the free neutral atoms. With this convention, the cohesive energy is a negative quantity. The exact Hartree-Fock cohesive energy is denoted by $\epsilon_{\text{HF}}^{\text{coh}}$. Since the analysis to be presented is somewhat intricate, we have included a list of all the notation in an Appendix, which also provides a brief summary of the steps involved in our practical formula for $\epsilon_{\text{HF}}^{\text{coh}}$.

Hartree-Fock Cohesive Energy with Pseudopotentials

As a start, we calculate the HF cohesive energy using pseudopotentials, denoting this by $\epsilon_{\text{ps}}^{\text{coh}}$. We show first that the HF pseudo-energy of the perfect crystal can be calculated to high precision.

We use the Hartree-Fock pseudopotentials created by the group of Needs.²⁷ Technically, they are Dirac-Fock Average Relativistic Effective Potentials (AREP's). When used in Hartree-Fock calculations, they are constructed so as to reproduce (approximately) all-electron Hartree-Fock results. Further details of their properties, and how they are generated are given in ref. 27. It is important for later purposes to note that each of these pseudopotentials comes in two forms. The primary form is a finely spaced numerical table of the pseudopotential as a function of radial distance r for each angular momentum. However, in order to facilitate the use of the pseudopotentials in quantum chemistry codes, a representation of the radial form for each angular momentum is also given in terms of a superposition of Gaussians multiplied by powers of r . These two representations of each pseudopotential are, of course, not identical, because the superposition of Gaussians is only an approximation to the primary (tabulated) form. The Gaussian representation is carefully constructed so as to be as accurate as possible, but it is still not exact. The calculations to be presented below use both forms, which we refer to as “tabulated” and “Gaussian-fit”. The pseudopotentials used for H and Li are publicly available.²⁸

Calculations on Periodic Systems

Using the PWSCF code,²² we start by studying convergence with respect to k -points and plane-wave cut-off. We first report results for LiH using tabulated pseudopotentials at the lattice parameter $a_0 = 4.084$ Å, which is the equilibrium value at room temperature. Table 1 shows that a plane-wave cut-off of 125 E_h and a $5 \times 5 \times 5$ Monkhorst-Pack k -point sampling grid suffice to ensure that the HF pseudo-energy of the crystal is converged to better than 5 μ E_h per ion pair, and these settings for cut-off and k -grid will be used in all the following calculations, unless otherwise specified. Additional tests on plane-wave cut-off, which confirm this convergence, will be mentioned below in Section Hartree-Fock Pseudo-Energy of Free Atoms. In the pseudopotential approximation, the cohesive energy $\epsilon_{\text{ps}}^{\text{coh}}$ is the difference between the HF pseudo-energy of the crystal per Li-H pair and the sum of the HF pseudo-energies of the free atoms. Since we can calculate the HF pseudo-energies of the atoms

Table 1. Calculated Hartree-Fock Pseudo-Energy $E_{\text{HF}}^{\text{ps}}$ Per Li-H Pair in LiH Crystal as Function of Plane-Wave Cut-Off Energy E_{cut} and Monkhorst-Pack k -Points Grid.

$E_{\text{cut}} (E_h)$	k -pts	$E_{\text{HF}}^{\text{ps}} (E_h)$
125	$4 \times 4 \times 4$	-0.829911
125	$5 \times 5 \times 5$	-0.829877
125	$6 \times 6 \times 6$	-0.829873
150	$4 \times 4 \times 4$	-0.829912

Results are for lattice parameter $a_0 = 4.084 \text{ \AA}$.

very precisely (see below), the results of Table 1 imply that we can calculate the Hartree-Fock part of the cohesive energy in the pseudopotential approximation to high precision.

For later purposes, it is useful to compare results obtained with the tabulated and Gaussian-fit versions of the Li and H pseudopotentials. Here, a bit of explanation is needed. The PWSCF code requires pseudopotentials to be presented in the form of radial tables. This means that in order to run the code using the Gaussian-fit form of the pseudopotentials, we must first construct radial tables of this Gaussian-fit form. We shall refer to this tabular representation of the Gaussian-fit pseudopotentials as “tabulated-Gaussian” pseudopotentials. Table 2 compares the Hartree-Fock pseudo-energies at four different lattice parameters calculated with the “tabulated” and “tabulated-Gaussian” pseudopotentials. The comparison shows that the differences vary from ~ 0.3 to $\sim 0.6 \text{ m}E_h$, which is not negligible for present purposes.

Hartree-Fock Pseudo-Energy of Free Atoms

To obtain the HF cohesive energy in the pseudopotential approximation, we need to calculate the HF pseudo-energies of the free atoms. In explaining how we have done this, we shall go to what may appear absurd lengths to compare several different methods. The reason for going to such lengths is that the methods that we now describe will be important also in calculating the pseudopotential error (Section Correcting for the Pseudopotential Error).

Our first method for calculating the pseudo-Hartree-Fock energy of the atoms is to apply PWSCF to a periodic system in which the repeating cell contains a single atom, and the dimensions of the cell are increased until interactions between images in different cells are negligible. This approach can be used both for the “tabulated” and “tabulated-Gaussian” forms of the pseudopotential. Our second method makes use of the fact that the MOLPRO code can be used to calculate the Hartree-Fock energy with pseudopotentials, so long as these are presented in Gaussian form. We have also used a third, less obvious method, which makes use of our ability to perform quantum Monte Carlo calculations²⁹ on systems with or without periodic boundary conditions (pbc). If we perform variational Monte Carlo calculations, using a Slater determinant of single-electron orbitals obtained with PWSCF, then the total energy obtained is the pseudo-Hartree-Fock energy. We have done calculations of this kind using the CASINO code.³⁰ Since these calculations can be done on a given system either with or without pbc, we have here a useful way of directly determining the errors due to the use of pbc.

Table 2. Comparison of Hartree-Fock Pseudo-Energies $E_{\text{HF}}^{\text{ps}}$ (E_h units) Per Ion Pair in LiH Crystal Calculated With Tabulated and Gaussian-fit Pseudopotentials.

$a_0 (\text{Å})$	tab	Gauss
3.684	-0.823415	-0.822785
3.884	-0.828523	-0.828034
4.084	-0.829877	-0.829498
4.284	-0.828540	-0.828248

Results are given at different values of the lattice parameter a_0 . Calculations use plane-wave cut-off $E_{\text{cut}} = 125 E_h$ and $5 \times 5 \times 5 k$ -point sampling.

We report in Table 3 results for the HF pseudo-energies of the H and Li atoms, obtained by our three methods, using, wherever possible, both the tabulated and the Gaussian forms of the pseudopotentials. The PWSCF calculations were all performed with Γ -point sampling and with a plane-wave cut-off of $125 E_h$. It is worth mentioning that for the PWSCF calculations on H, we have taken the opportunity to conduct additional tests on the plane-wave cut-off E_{cut} . We find that as E_{cut} is increased from 125 to 350 E_h , the calculated pseudo-energy of the atom decreases by only $14 \mu E_h$, the change on going from 250 to 350 E_h being only $4 \mu E_h$. This confirms that $E_{\text{cut}} = 125 E_h$ is more than adequate for present purposes. For the MOLPRO calculations, we have used standard Dunning cc-pVnZ basis sets,^{31,32} but uncontracted so that all Gaussian primitives are independent. Results obtained in this way for VTZ, VQZ, and V5Z sets are then extrapolated to the basis-set limit using the three-point exponential formula discussed recently for Hartree-Fock calculations by Jensen,³³ according to which the HF energy $E(L_{\text{max}})$ obtained with a cc-pVnZ basis whose maximum angular momentum is L_{max} is $E(L_{\text{max}}) = A + B \exp(-CL_{\text{max}})$. The results show that for either form of the pseudopotentials, the HF pseudo-energy can readily be determined to a precision of $\sim 50 \mu E_h$.

Table 3. Hartree-Fock Pseudo-Energies (E_h units) of Free H and Li Atoms, Calculated Using the PWSCF, CASINO, and Molpro Codes, and With Tabulated and Gaussian Pseudopotentials.

Calculation	H	Li
	Tabulated pseudopotentials	
PWSCF ($L = 20$ a.u.)	-0.499956	-0.197095
PWSCF ($L = 30$ a.u.)	-0.499956	-0.196352
PWSCF ($L = 40$ a.u.)	—	-0.196348
CASINO	-0.500024(2)	-0.196338(1)
	Gaussian pseudopotentials	
Molpro (VTZ)	-0.499689	-0.196247
Molpro (VQZ)	-0.499980	-0.196284
Molpro (V5Z)	-0.500003	-0.196300
Molpro (∞)	-0.500005	-0.196312
PWSCF	-0.499955	-0.196347

PWSCF calculations using Gaussian pseudopotentials were done with cell lengths of 30 and 40 a.u. for H and Li respectively.

Table 4. Hartree-Fock Pseudo-Energies (E_h units) of Selected Clusters Calculated in Periodic Boundary Conditions With PWSCF for different repeating cells.

Cluster	PWSCF					CASINO
$1 \times 1 \times 2$	$20 \times 20 \times 20$ −0.737927	$25 \times 25 \times 25$ −0.736835	$30 \times 30 \times 30$ −0.736408	$35 \times 35 \times 35$ −0.736179	$40 \times 40 \times 40$ −0.736050	−0.73579(1)
$1 \times 2 \times 2$	$20 \times 20 \times 20$ −1.556938	$25 \times 25 \times 25$ −1.556336	$30 \times 30 \times 30$ −1.556155	$35 \times 35 \times 35$ −1.556089	$40 \times 40 \times 40$ −1.556062	−1.55605(2)
$2 \times 2 \times 2$	$20 \times 20 \times 20$ −3.201782	$25 \times 25 \times 25$ −3.201531	$30 \times 30 \times 30$ −3.201461	$35 \times 35 \times 35$ −3.201445	$40 \times 40 \times 40$ −3.201440	−3.20135(4)
$1 \times 4 \times 4$	$20 \times 26 \times 26$ −6.428209	$25 \times 32 \times 32$ −6.425594	$30 \times 39 \times 39$ −6.424849	$35 \times 45 \times 45$ −6.424584	$40 \times 52 \times 52$ −6.424479	−6.42407(6)
$2 \times 2 \times 4$	$20 \times 20 \times 20$ −6.476855	$25 \times 25 \times 25$ −6.472651	$30 \times 30 \times 30$ −6.472199	$30 \times 30 \times 39$ −6.472117	$35 \times 35 \times 35$ −6.472108	−6.47166(8)

The cells are orthorhombic, and their dimensions are given in the form $L_1 \times L_2 \times L_3$ (edge lengths L_α in a.u.). Right-most column gives HF pseudo-energy obtained from CASINO calculations on free clusters. All results are for tabulated pseudopotentials.

Correcting for the Pseudopotential Error

As indicated in the Introduction, we determine the pseudopotential error by comparing the formation energies of free clusters calculated with the pseudopotential approximation and with all-electron calculations. In this Section, we describe first how we have calculated the formation energies of clusters using pseudopotentials, and then how we have done the same thing with all-electron calculations. In the final part of the Section, we outline the hierarchical analysis used to extract the pseudopotential error for the bulk crystal. This analysis allows us to obtain highly converged values of the Hartree-Fock cohesive energy of the crystal at different lattice parameters.

Pseudopotential Calculations on Free Clusters

The three methods used to calculate the pseudo-Hartree-Fock energies of the free atoms can all be applied for the same purpose to clusters. We regard a careful comparison of the results of the different methods as extremely important. The reason is that our whole strategy for calculating the HF cohesive energy relies on a combination of completely different technologies, namely pseudopotentials with plane waves (PWSCF) and all-electron calculations with Gaussians (Molpro). Since we are trying to attain a precision of better than $1 mE_h$ /atom it is clear that even very small inconsistencies between the different technologies can prevent us from attaining our goal. In this sense, the ability to compare the pseudo-HF energies of a hierarchy of clusters obtained with PWSCF and with Molpro can give us much needed reassurance that such inconsistencies are not significantly affecting the results.

We first apply our methods to all neutral LiH clusters containing up to 16 ions. For present purposes, a “cluster” is a cuboidal piece of the rock-salt structured crystal, whose edges are parallel to the cubic crystal axes and contain l , m , and n ions. We refer to such a cluster as an $l \times m \times n$ cluster. For electro-neutrality, the product lmn must be even. The smallest such cluster is $1 \times 1 \times 2$, which is the LiH molecule. All the calculations in which we compare the different methods are done with the Li-H nearest-neighbour distance $d = \frac{1}{2}a_0 = 2.042 \text{ \AA}$.

In using the PWSCF code to obtain pseudo-HF energies of the free clusters, we must, of course, pay careful attention to the errors due to the use of periodic boundary conditions. As expected, the $1 \times 1 \times 2$ cluster is the one that converges most slowly with respect to cell size, since it is the only cluster that has a dipole moment. However, since we know that the cell-size error for the $1 \times 1 \times 2$ cluster must decay as $1/L^3$, it is straightforward to remove the leading term in this error by extrapolation. As a cross-check on the cell-size errors, we have performed CASINO calculations without pbc. We compare in Table 4 the HF pseudo-energies obtained with PWSCF and CASINO, using tabulated pseudopotentials. The comparisons show that the HF pseudo-energies of clusters can be calculated to a precision of $\sim 50 \mu E_h$ per ion pair.

We now report the pseudopotential calculations on all neutral clusters having up to 16 ions using Molpro. We have used the same fully decontracted Dunning basis sets as were used for our calculations on the free atoms (Section Hartree-Fock Pseudo-Energy of Free Atoms). We show in Table 5 the resulting pseudo-HF formation energies (relative to free atoms), compared with those obtained from PWSCF using the Gaussian pseudopotentials. The free-atom pseudo-HF energies used to obtain all the results in the Table were $-0.499956 E_h$ for H and $-0.196348 E_h$ for Li (see Table 3). As a measure of the basis-set errors in the Molpro results, we list the quantities $2(E_{\text{form}}(V\infty Z) - E_{\text{form}}(VnZ))/N$, where $N = lmn$ is the number of ions in the cluster, denoting these by δ_T , δ_Q and δ_5 , according to whether the basis set is triple-, quadruple- or quintuple-zeta. The δ -values indicate that with VTZ, VQZ and V5Z, the basis-set errors per ion pair are almost constant at -0.45 , -0.08 , and $-0.015 mE_h$ respectively.

All-Electron Calculations on Free Clusters

Our HF all-electron calculations on free clusters were all performed using the standard Dunning basis sets.^{31,32} (Our tests on the effect of decontracting the basis sets indicate that the improvement is insignificant.) To show the basis-set convergence, we report in Table 6 the all-electron HF formation energies of all clusters up to 16 ions, obtained with VTZ, VQZ, and V5Z basis sets, as well as the extrapolated values obtained by the three-point exponential

Table 5. HF Pseudo-Formation Energies (E_h units) of Li-H Clusters Obtained from Molpro With Different Decontracted Dunning Basis Sets, and Values Obtained by Extrapolation to Basis-Set Limit.

Cluster	Molpro				PWSCF	δ_T	δ_Q	δ_5
	VTZ	VQZ	V5Z	$V\infty Z$				
$1 \times 1 \times 2$	-0.038942	-0.039354	-0.039441	-0.039464	-0.03943	-0.522	-0.110	-0.023
$1 \times 2 \times 2$	-0.162266	-0.163057	-0.163210	-0.163247	-0.16318	-0.491	-0.095	-0.019
$1 \times 2 \times 3$	-0.271008	-0.272150	-0.272347	-0.272388	-	-0.460	-0.079	-0.014
$1 \times 2 \times 4$	-0.384287	-0.385766	-0.386011	-0.386060	-0.38629	-0.443	-0.074	-0.012
$1 \times 2 \times 5$	-0.495737	-0.497572	-0.497869	-0.497926	-	-0.438	-0.071	-0.011
$1 \times 2 \times 6$	-0.608092	-0.610285	-0.610637	-0.610704	-	-0.435	-0.070	-0.011
$1 \times 2 \times 7$	-0.719907	-0.722457	-0.722865	-0.722943	-	-0.434	-0.069	-0.011
$1 \times 2 \times 8$	-0.832060	-0.834970	-0.835434	-0.835522	-0.83586	-0.433	-0.069	-0.011
$1 \times 3 \times 4$	-0.607733	-0.609951	-0.610309	-0.610378	-	-0.441	-0.071	-0.012
$1 \times 4 \times 4$	-0.848890	-0.851825	-0.852298	-0.852389	-0.85262	-0.437	-0.071	-0.011
$2 \times 2 \times 2$	-0.413537	-0.415051	-0.415349	-0.415422	-0.41545	-0.471	-0.093	-0.018
$2 \times 2 \times 3$	-0.653911	-0.656175	-0.656591	-0.656685	-	-0.462	-0.085	-0.016
$2 \times 2 \times 4$	-0.896014	-0.899000	-0.899537	-0.899655	-0.89984	-0.455	-0.082	-0.015

Results are compared with PWSCF values obtained in periodic boundary conditions with large cells. All values refer to Gaussian pseudopotentials. Quantities δ_T , δ_Q , and δ_5 are estimates of Molpro basis-set errors per ion pair (mE_h units).

formula mentioned earlier. (The HF energies of the free atoms used here are $-0.5 E_h$ for H and $-7.432727 E_h$ for Li, the latter value being within $1 \mu E_h$ of the HF limit.³⁴) We also give the quantities $2(E_{\text{form}}(\infty) - E_{\text{form}}(VnZ))/N$, where $E_{\text{form}}(VnZ)$ is the formation energy using the VnZ basis set, and $E_{\text{form}}(\infty)$ is the value obtained by extrapolation, denoting these quantities by δ_T , δ_Q , and δ_5 , according to the basis set. We deduce from this that the errors in all-electron formation energy per ion pair with triple-zeta, quadruple-zeta and quintuple-zeta basis sets are almost constant at 0.5, 0.14, and 0.040 mE_h . The implication is that if we can calculate the all-electron HF total energy of the bulk crystal at the VTZ, VQZ, and V5Z levels, then we can correct the results using these (almost) constant values of the basis-set errors, and the corrected results should be within ~ 100 , ~ 10 and $\sim 5 \mu E_h$ of the basis-set limit, respectively.

Hierarchy Analysis to Determine Pseudopotential Errors

The results presented above show that Molpro calculations of the pseudo-HF formation energies of clusters agree to high precision with the formation energies calculated with PWSCF (and CASINO), and that Molpro can also give highly converged all-electron values of the cluster formation energies. This means that we can now calculate the difference between all-electron-HF and pseudo-HF formation energies of clusters using only Molpro. We denote this difference (all-electron minus pseudo) for the $l \times m \times n$ cluster by $\Delta E_{lmn}^{\text{form}}$. We now need a systematic way of extracting the correction for the pseudopotential error in the cohesive energy of the bulk crystal. To do this, we use a procedure closely resembling the hierarchical analysis that we used elsewhere¹² to calculate the ‘‘correlation residual’’ contribution to the cohesive energy.

Table 6. All-Electron HF Formation Energies (E_h units) of Li-H Clusters Calculated Using Dunning VTZ, VQZ, and V5Z Basis sets, With the Value Obtained by Exponential Extrapolation Denoted by $V\infty Z$.

Cluster	VTZ	VQZ	V5Z	$V\infty Z$	δ_T	δ_Q	δ_5
$1 \times 1 \times 2$	-0.039279	-0.039711	-0.039854	-0.039925	-0.646	-0.214	-0.071
$1 \times 2 \times 2$	-0.162161	-0.162997	-0.163220	-0.163301	-0.570	-0.152	-0.041
$1 \times 2 \times 3$	-0.270337	-0.271448	-0.271750	-0.271863	-0.509	-0.138	-0.038
$1 \times 2 \times 4$	-0.383110	-0.384504	-0.384891	-0.385040	-0.483	-0.134	-0.030
$1 \times 2 \times 5$	-0.494042	-0.495742	-0.496217	-0.496401	-0.472	-0.132	-0.037
$1 \times 2 \times 6$	-0.605878	-0.607886	-0.608452	-0.608674	-0.466	-0.131	-0.037
$1 \times 2 \times 7$	-0.717176	-0.719494	-0.720150	-0.720409	-0.462	-0.131	-0.037
$1 \times 2 \times 8$	-0.828811	-0.831440	-0.832187	-0.832483	-0.459	-0.130	-0.037
$1 \times 3 \times 4$	-0.605239	-0.607231	-0.607798	-0.608024	-0.464	-0.132	-0.038
$1 \times 4 \times 4$	-0.845155	-0.847760	-0.848509	-0.848811	-0.457	-0.131	-0.038
$2 \times 2 \times 2$	-0.412161	-0.413867	-0.414291	-0.414431	-0.568	-0.141	-0.035
$2 \times 2 \times 3$	-0.651221	-0.653543	-0.654153	-0.654370	-0.525	-0.138	-0.036
$2 \times 2 \times 4$	-0.892033	-0.895004	-0.895799	-0.896089	-0.507	-0.136	-0.036

Also shown are the differences $\delta_n = 2(E_{\text{form}}(\infty) - E_{\text{form}}(VnZ))/N$ (mE_h units) for the three basis sets, with N the number of ions in the cluster.

The correction $\Delta\varepsilon^{\text{coh}}$ per ion pair that must be added to the cohesive energy calculated with pseudopotentials is the limit of $2\Delta E_{lmn}^{\text{form}}/lmn$ as l, m and $n \rightarrow \infty$. For clusters of a size that can be handled with Molpro, there are likely to be substantial contributions to $\Delta E_{lmn}^{\text{form}}$ from the surfaces (and perhaps from edges and corners) of clusters, so we cannot assume that the limiting value of $2\Delta E_{lmn}^{\text{form}}/lmn$ will be correctly obtained by simple extrapolation. However, we can assume that in the limit of large clusters $\Delta E_{lmn}^{\text{form}}$ will go to the asymptotic form:

$$\Delta E_{lmn}^{\text{form}} \rightarrow e^{000} + e^{001}(l + m + n) + e^{011}(mn + nl + lm) + e^{111}lmn, \quad (1)$$

where the coefficients e^{111} , e^{011} , e^{001} , and e^{000} are associated with the bulk, surfaces, edges and corners, respectively. The coefficient that concerns us most here is e^{111} , since the required correction is $\Delta\varepsilon^{\text{coh}} = 2e^{111}$.

Following our earlier ideas,¹² we note now that if we have the values of $\Delta E_{lmn}^{\text{form}}$ for four different clusters, we can solve the four simultaneous equations (1) to obtain estimates of the four coefficients e^{000} , e^{001} , e^{011} , and e^{111} . This can be done, provided the four equations are linearly independent. We must therefore require that the four clusters be chosen so that the determinant whose rows are made of the coefficients 1, $l + m + n$, $mn + nl + lm$ and lmn does not vanish. As a short-hand, we call these “linearly independent clusters.” For any given set of four clusters, the coefficients so obtained are only estimates, and we need to find the limits to which the estimates tend as we go to infinite clusters. The “hierarchical” procedure we have developed for doing this works as follows. We choose an even integer N , and we make the complete list of all neutral clusters for which the total number of ions is less than or equal to N . In making this list, we do not count as distinct clusters whose indices l, m , and n differ only by permutations, so that we can take the list to consist of triplets (l, m, n) for which $l \leq m \leq n$. The clusters in the list are arranged in lexicographical order, which means that if we have two clusters (l_1, m_1, n_1) and (l_2, m_2, n_2) then (l_1, m_1, n_1) precedes (l_2, m_2, n_2) if:

- $l_1 < l_2$
- $l_1 = l_2$ and $m_1 < m_2$
- $l_1 = l_2$ and $m_1 = m_2$ and $n_1 < n_2$.

As we pass through the list, n varies most rapidly, followed by m and then l . With this ordering, the clusters that come towards the end of the list are those for which l, m , and n are all large.

Using the lexicographical list constructed for a given integer N , we now make a procedure for choosing four large linearly independent clusters. The last two members of the lexicographical list are always chosen, since it can be shown that they are guaranteed to be linearly independent. However, as we continue to count back in the list, the next member is not necessarily linearly independent of the two already chosen. If it is linearly independent, we choose it, but otherwise we continue to count back until we find a member that is linearly independent. We do the same thing to find the fourth and final member. Solution of the four simultaneous equations now gives us values of the coefficients. These values depend, of course, on the integer N that was initially chosen. To go to the asymptotic

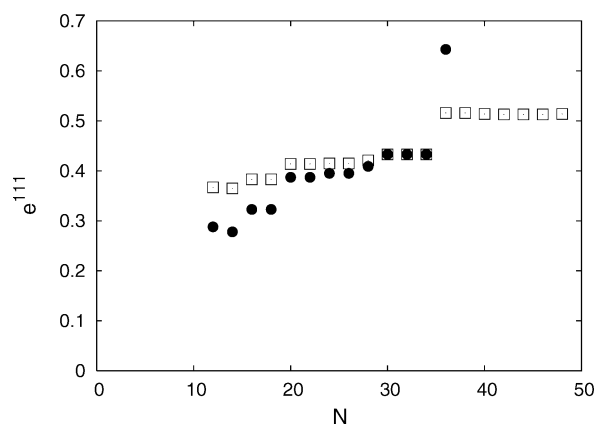


Figure 1. Coefficient e^{111} (mE_h units) characterizing difference between all-electron HF and pseudo-HF formation energies of LiH clusters as function of N in hierarchical analysis (see text). Results are shown for VTZ (open squares) and VQZ (closed circles) basis sets.

limit, we now repeat this procedure for increasing N values until the coefficients are converged to the required tolerance.

To apply this analysis, we have calculated $\Delta E_{lmn}^{\text{form}}$ for all clusters containing up to 48 ions, using VTZ basis sets for both all-electron and pseudopotential calculations, and for all clusters up to 36 ions with VQZ basis sets for both. The resulting values of e^{111} obtained with the VTZ basis set (Fig. 1) show plateaux separated by small breaks. For the smallest values of N , there are no atoms in bulk environments, so the results are not necessarily meaningful. The smallest cluster for which there are atoms in bulk environments is $3 \times 3 \times 4$, and we therefore believe that the plateau for $N \geq 36$ represents a close approximation to the asymptotic e^{111} . For the VQZ basis set, we have gone only to $N = 36$, and we regard the e^{111} for this N as the best available value for this basis set. Denoting the values of e^{111} obtained with VTZ and VQZ basis sets by $e^{111}(\text{VTZ})$ and $e^{111}(\text{VQZ})$, we find the asymptotic values to be $e^{111}(\text{VTZ}) = 0.51 mE_h$ and $e^{111}(\text{VQZ}) = 0.64 mE_h$.

Final Hartree-Fock Results

We now assemble all the foregoing results, to obtain an accurate value of the Hartree-Fock cohesive energy $\varepsilon_{\text{HF}}^{\text{coh}}$ relative to free atoms. The notation used for all the quantities that enter the calculation is summarised in the Appendix, where we show that the final value of $\varepsilon_{\text{HF}}^{\text{coh}}$ obtained when we use all-electron and pseudopotential cluster calculations with VnZ basis sets to estimate the pseudopotential correction is given by:

$$\varepsilon_{\text{HF}}^{\text{coh}} = \varepsilon_{\text{ps}}^{\text{coh}}(\text{PWSCF}) + \varepsilon_{\text{ps}}^{\text{coh}}(\text{Molpro-PWSCF}) + 2e^{111}(VnZ) + \delta_{\text{BSE}}(\text{AE}, VnZ) - \delta_{\text{BSE}}(\text{ps}, VnZ). \quad (2)$$

The numerical results to be presented now refer to the lattice parameter $a_0 = 4.084 \text{ \AA}$. From Section Hartree-Fock Pseudo-Energy of Free Atoms, the pseudopotential approximation to the HF cohesive energy given by PWSCF is $\varepsilon_{\text{ps}}^{\text{coh}}(\text{PWSCF}) = -133.19 mE_h$. We have seen from our pseudopotential calculations

Table 7. Calculated Hartree-Fock Equilibrium Values of the Cohesive Energy $\epsilon_{\text{HF}}^{\text{coh}}$, the Lattice Parameter a_0 and the Bulk Modulus B .

	$\epsilon_{\text{HF}}^{\text{coh}}$ (mE_h)	a_0 (Å)	B (GPa)
VTZ	-132.23	4.1051	32.82
VQZ	-131.99	4.1084	32.05
CRYSTAL	-129.14(-130.16)	4.121	28.3

Results are corrected for pseudopotential error using hierarchy analysis on cluster calculations performed with VTZ and VQZ basis sets. The results are compared with published values obtained with the CRYSTAL code, the values without and with brackets being from refs. 11 and 36 respectively.

on clusters that the PWSCF and Molpro treatments of Gaussian pseudopotentials give almost identical results, the difference per ion pair being $\epsilon_{\text{ps}}^{\text{coh}}$ (Molpro-PWSCF) = 0.02 mE_h .

We saw in Section Hierarchy Analysis to Determine Pseudopotential Errors that our calculations with VTZ basis sets give a correction for the cohesive energy per ion pair e^{111} (VTZ) = 0.51 mE_h . We also saw there that the basis-set corrections in this case are $\delta_{\text{BSE}}(\text{AE, VTZ}) = -0.51 mE_h$ and $\delta_{\text{BSE}}(\text{ps, VTZ}) = -0.46 mE_h$. Putting these results together, we obtain the corrected cohesive energy $\epsilon_{\text{HF}}^{\text{coh}} = -132.20 mE_h$. On the other hand, with VQZ basis sets, we obtained e^{111} (VQZ) = 0.64 mE_h , $\delta_{\text{BSE}}(\text{AE, VQZ}) = -0.14 mE_h$ and $\delta_{\text{BSE}}(\text{ps, VQZ}) = -0.08 mE_h$, so that the final cohesive energy in this case is $\epsilon_{\text{HF}}^{\text{coh}} = -131.95 mE_h$. The final results obtained using VTZ and VQZ basis sets to correct for the pseudopotential errors are therefore within 0.2 mE_h of each other. We believe that the VQZ result is to be preferred.

We have repeated the calculations at a number of values of lattice parameter a_0 , in order to obtain HF values of the equilibrium lattice parameter and bulk modulus. More precisely, we have performed pseudopotential-plane-wave calculations of the HF pseudopotential cohesive energy $\epsilon_{\text{ps}}^{\text{coh}}$ at a_0 values ranging from 3.684 to 4.284 Å at intervals of 0.1 Å, using in all cases the plane-wave cut-off of 125 E_h and $5 \times 5 \times 5$ k -point sampling. To obtain the pseudopotential error as a function of lattice parameter, we have performed all-electron and pseudopotential calculations on the four clusters $2 \times 3 \times 5$, $2 \times 3 \times 6$, $2 \times 4 \times 4$ and $3 \times 3 \times 4$, with both VTZ and VQZ basis sets, as described above, at lattice parameters $a_0 = 3.884$, 4.084, and 4.284 Å, and used the hierarchy analysis to obtain e^{111} in each case. A quadratic fit was then used to obtain e^{111} as a function of a_0 . This quadratic approximation to e^{111} allows us to obtain $\epsilon_{\text{HF}}^{\text{coh}}$ at the set of a_0 values from 3.684 to 4.284 Å at intervals of 0.1 Å. Finally, we performed a 3rd-order Birch-Murnaghan³⁵ fit to these results to obtain the equilibrium lattice parameter, the cohesive energy at this a_0 , and the bulk modulus B . We compare the results with those from published CRYSTAL calculations^{11,36} in Table 7. (In making the comparison for $\epsilon_{\text{HF}}^{\text{coh}}$, we have taken from refs. 36 and 11 the values -8.06289 and $-8.06187 E_h$ for the total Hartree-Fock energy of the crystal per ion pair. These have then been converted to cohesive energies relative to free atoms, using the essentially exact Hartree-Fock energies of the H and Li atoms, which are -0.5 and $-7.432727 E_h$.)

Given that the original CRYSTAL calculations³⁶ of Hartree-Fock cohesive energy of LiH were reported over 20 years ago, they are in remarkable agreement with our values. The reason why the very

recent repetition of the CRYSTAL calculations¹¹ gives a Hartree-Fock energy that is higher than the old value by $\sim 1 mE_h$ is unclear. To check this, we have performed our own CRYSTAL calculations, using exactly the same Gaussian basis set used by Dovesi *et al.*,³⁶ obtaining the total energy $-8.06169 E_h$, which is indeed above the old value by 1.2 mE_h . However, we find that on expanding the basis set the energy can be lowered to $-8.06326 E_h$, giving $\epsilon_{\text{HF}}^{\text{coh}} = -0.13053 E_h$, which is still above our value by 1.5 mE_h . Since the margin of error on our value appears to be much smaller than this, we believe that the difference is significant, and that it is due to residual basis-set incompleteness in CRYSTAL. Whether the differences in the equilibrium values of a_0 and B are significant is debatable.

Discussion and Conclusions

Our results for the Hartree-Fock cohesive energy $\epsilon_{\text{HF}}^{\text{coh}}$ of LiH show the possibility of calculating this quantity to a precision approaching 0.1 mE_h /atom, at least for this material. We recall that in conventional methods based on the use of Gaussian basis sets the attainable precision is limited mainly by the difficulty of achieving basis-set convergence, and specifically by the instabilities caused by near linear dependence of the basis functions. Comparison with literature values of $\epsilon_{\text{HF}}^{\text{coh}}$ for LiH suggests that with Gaussians it is difficult to achieve convergence to better than 1 mE_h /atom. In effect, our strategy transfers the difficulty from one place to another. We have shown that, with plane waves and pseudopotentials, basis-set convergence to arbitrarily high precision is straightforward; for example, convergence to within 1 μE_h could readily be attained. However, the difficulty is now to converge the difference between the pseudopotential and all-electron cohesive energy per atom with respect to cluster size. In the case we have studied, the pseudopotentials appear to be very transferable, so that this difference is very small, and size convergence is not hard to achieve.

However, LiH is clearly a favorable case, because it has a very simple crystal structure and the number of electrons per atom is small. It is important to ask what difficulties will arise if we apply our strategy to other materials. For many materials having the same rock-salt structure, our strategy will be applicable without change, and we hope to report calculations on such materials soon. The calculations will necessarily be heavier than for LiH, but the pseudopotential HF cohesive energy should still be calculable to arbitrary precision. It may be that the differences between pseudopotential and all-electron energies of clusters for these materials will be larger. However, we note that the methods we have used here to converge this difference are still very crude, since we have used completely free clusters, for which the surface energy is a large contribution. It should be possible to achieve far better size convergence using embedded clusters, and we plan to study this.

There is also another development that seems very promising. We have noted the possibility of calculating the Hartree-Fock energy of crystals with the projector augmented-wave (PAW) scheme,¹⁸ which is closely related to the ultra-soft pseudopotential method with plane-wave basis sets. If required, full core relaxation²¹ can also be applied. This PAW scheme may well be able to approach the exact all-electron limit more closely than pseudopotential methods, in which case correction for the difference between the PAW and exact values of the HF energy may become unnecessary. We suggest that

the strategies outlined here could be important in assessing whether this is the case.

In conclusion, we have presented a strategy for calculating the Hartree-Fock energy of crystals with high precision, and have demonstrated the effectiveness of this strategy for LiH. We have noted the need to test the strategy on other, more challenging materials, and have also pointed out ways of improving the strategy.

Acknowledgments

The work of FRM was supported by the Royal Society, and of DA was conducted as part of a EURYI scheme award. We thank S. Taioli for performing CRYSTAL calculations.

Appendix: Notation

Here, we provide a summary of the notation used in the calculation of the Hartree-Fock cohesive energy. The cohesive energy of the bulk crystal and the formation energies of cluster are always defined relative to free atoms. The cohesive and formation energies are always defined to be energy of crystal (or cluster) minus energy of equivalent number of atoms, so that they are negative quantities. Note also that the energies of free atoms that enter the following quantities are always taken to be calculated at the basis-set limit (pseudopotential or all-electron as appropriate), even if the quantity refers to the energy of a cluster treated with a finite basis set.

- $\varepsilon_{\text{HF}}^{\text{coh}}$: Exact Hartree-Fock cohesive energy per ion pair (energy of crystal minus energy of neutral atoms).
- $\varepsilon_{\text{ps}}^{\text{coh}}$ (PWSCF): cohesive energy per ion pair calculated for perfect crystal using PWSCF at basis-set limit. (Necessarily employs pseudopotential.)
- $\varepsilon_{\text{ps}}^{\text{coh}}$ (Molpro): Hypothetical cohesive energy per ion pair that would be obtained for perfect crystal using Molpro at basis-set limit, using pseudopotentials. One can think of this as formation energy of cluster per ion pair at basis-set limit, in limit of infinite cluster.
- $\varepsilon_{\text{ps}}^{\text{coh}}$ (Molpro–PWSCF): Defined as the difference $\varepsilon_{\text{ps}}^{\text{coh}}$ (Molpro) – $\varepsilon_{\text{ps}}^{\text{coh}}$ (PWSCF).
- E_{lmn}^{form} (PWSCF): formation energy of $l \times m \times n$ cluster (total energy of cluster minus total energy of free atoms) calculated with PWSCF employing pseudopotentials at basis-set limit.
- E_{lmn}^{form} (ps, VnZ): formation energy of $l \times m \times n$ cluster from free atoms, calculated with Molpro employing pseudopotentials and VnZ basis set. Value obtained by basis-set extrapolation using 3-point exponential formula is denoted by $V\infty Z$.
- E_{lmn}^{form} (AE, VnZ): same as E_{lmn}^{form} (ps, VnZ), but with all-electron calculations.
- δ_{BSE} (ps, VnZ): basis-set error per ion pair in formation energy of cluster obtained with VnZ basis set, employing pseudopotential. Defined as energy at basis-set limit minus energy with VnZ : δ_{BSE} (ps, VnZ) = $2(E_{lmn}^{\text{form}}$ (ps, $V\infty Z$) – E_{lmn}^{form} (ps, VnZ))/ N , where $N = lmn$ is number of ions in cluster.
- δ_{BSE} (AE, VnZ): same as δ_{BSE} (ps, VnZ), but with all-electron calculations.

- e^{111} (VnZ): value of pseudopotential correction energy per ion obtained from hierarchy analysis, defined as:

$$\lim_{\text{cluster} \rightarrow \infty} [E_{lmn}^{\text{form}}(\text{AE}, VnZ) - E_{lmn}^{\text{form}}(\text{ps}, VnZ)]/N,$$

where $N = lmn$ is number ions in cluster. Note that e^{111} (VnZ) is defined per ion, not per ion pair.

With these definitions, the formula for the corrected value of the HF cohesive energy is:

$$\varepsilon_{\text{HF}}^{\text{coh}} = \varepsilon_{\text{ps}}^{\text{coh}}(\text{PWSCF}) + \varepsilon_{\text{ps}}^{\text{coh}}(\text{Molpro} - \text{PWSCF}) + 2e^{111}(VnZ) + \delta_{\text{BSE}}(\text{AE}, VnZ) - \delta_{\text{BSE}}(\text{ps}, VnZ).$$

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