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Accurate Hartree-Fock energy of extended systems using large Gaussian basis sets

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Calculating highly accurate thermochemical properties of condensed matter via wave-function-based approaches (such as, e.g., Hartree-Fock or hybrid functionals) has recently attracted much interest. We here present two strategies providing accurate Hartree-Fock energies for solid LiH in a large Gaussian basis set and applying periodic boundary conditions. The total energies were obtained using two different approaches, namely, a supercell evaluation of Hartree-Fock exchange using a truncated Coulomb operator and an extrapolation toward the full-range Hartree-Fock limit of a Padé fit to a series of short-range screened Hartree-Fock calculations. These two techniques agreed to significant precision. We also present the Hartree-Fock cohesive energy of LiH (converged to within sub-millielectron volt) at the experimental equilibrium volume as well as the Hartree-Fock equilibrium lattice constant and bulk modulus.

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I. INTRODUCTION

The high-accuracy/cost ratio of Kohn-Sham density-functional theory[1,2] (KS-DFT) has been exhaustively demonstrated in the literature. In its early days, KS-DFT using the local-density approximation[1] was almost exclusively applied by the solid-state community. However, the advent of generalized gradient approximations (see, e.g., Refs. 3–5) to the exchange-correlation (XC) functional and the introduction of nonlocal Hartree-Fock (HF) exchange in hybrid functionals[6,7] paved the way for reasonably accurate applications to molecules as well.

Within the framework of KS-DFT it is relatively easy to achieve basis set convergence, and atomic forces can be calculated at little extra computational cost. This is of paramount importance in the calculation of high-temperature dynamical and thermodynamic properties by molecular-dynamics simulations. In particular, DFT statistical mechanics for both bulk materials and for surface processes is routinely feasible (see, e.g., Ref. 8, and references therein). The principle limitation of KS-DFT lies in the accuracy of the applied XC functional.

Discussing examples for some shortcomings of KS-DFT, it is well known that standard local and semilocal approximations to the XC functional do not yield accurate results for quasiparticle band gaps of semiconductors and insulators. Generally, they do not predict the correct adsorption sites and adsorption energies of molecules on metallic surfaces (for details see, e.g., Ref. 9, and references therein). Today's DFT practitioner is confronted with these shortcomings when choosing an XC functional for a specific application. Each contemporary density functional has its relative merits but at the same time drawbacks, which might impede finding an appropriate XC functional. Different density functionals have different merits and demerits, an unsatisfactory situation. These inadequacies of semilocal KS-DFT have stimulated some DFT groups to use wave-function-based methods to benchmark or correct DFT results. Note that other researchers are directly applying wave-function-based techniques to materials science problems (see, e.g., Ref. 10) using the CRYSTAL code but comparable assessments of the therein implemented HF method close to the basis set limit is still an open issue.

Dramatic improvements for many properties of molecules as well as solids can be achieved by mixing a fraction of nonlocal HF exchange (HFX) to the remaining part of semilocal DFT exchange. Since these functionals do not only depend on the electron density alone, but also on the KS single-particle wave functions, i.e., the orbitals, they are called *hybrid* functionals. Therefore, these hybrid functionals can be seen as "mixed" wave-function-based and semilocal DFT methods. We refer the reader to a recent review[11] of so-called screened hybrid functionals, as, e.g., the Heyd-Scuseria-Ernzerhof[12,13] (HSE) functional, which was proposed to extend the successes of hybrid functionals into condensed matter, by avoiding the problematic effects of long-range (LR) HFX (see Ref. 11, and references therein).

Besides the successes of screened HFX applied to condensed matter, the numerous methodological and algorithmic developments in the quantum-chemistry community and the steady increase in computers' efficiency induced a drive to conceive and implement even more involved wave-function-based techniques, as, e.g., local second-order Møller-Plesset perturbation theory (MP2),[14–16] (resolution of the identity) atomic orbital Laplace transformed MP2 (Refs. 17–19) and canonical MP2 (Refs. 20 and 21) for (infinitely) extended systems of various dimensionality and applied basis functions. Furthermore, recent reports in the literature on *ab initio* molecular dynamics on condensed matter[22] employing the HSE-screened hybrid functional illustrate that, depending on implementation details, basis set and system, wave-function-based techniques are also applicable to statistical mechanics calculations. These successful applications of wave-function methods to large systems show that they are able to tackle materials science problems with possibly much better accuracy than conventional density functionals.

Recently published HF and post-HF calculations on crystalline LiH have attracted much interest in the solid-state community.[23–25] These calculations represent a benchmark in terms of eliminating as many inaccuracies as possible while attempting to converge toward the so-called HF limit. The approach in question employs calculations on a hierarchical series of cluster models,[23,26] exploiting strengths and weaknesses of plane-wave pseudopotentials as well as local Gaussian basis sets. Accurate evaluation of the total HF energy, as well as cohesive energy in the HF approximation employing exclusively Gaussian basis sets is desirable to bypass errors incurred by the pseudopotential approximation. Admittedly, creating an all-electron Gaussian basis set, which describes the crystal as well as the isolated atoms equally well, is challenging. Referring to the arguments of Gillan *et al.*,[24] it is in general difficult to provide rigorous estimates how far the applied basis set is from the HF limit. However, it is reasonable to question the need for reaching the HF limit for particular materials properties, which is substantiated in the present work.

We compare total HF energies of solid LiH using two different codes employing Gaussian basis functions: (i) the Gaussian and augmented plane-wave[27] code CP2K/QUICKSTEP (Refs. 28 and 29) and (ii) a developmental version of the GAUSSIAN suite of programs.[30] We show that the cohesive energy of the crystal is converged to within sub-millielectron volt accuracy in our given large Gaussian basis set (see Table I). Computational and methodological details are presented in Sec. II. Results for cohesive energies, theoretical lattice constant as well as bulk modulus are in Sec. III. Conclusions are drawn in Sec. IV.

II. COMPUTATIONAL DETAILS

In the following sections, we describe important computational details, such as the Gaussian basis set, the evaluation of full-range HFX based on the short-range (SR) HFX implementation[31] in the GAUSSIAN suite of programs as well as the method applied for the extrapolation of the SR-HFX energy to the full-range limit based on Padé approximants. Furthermore, implementation details on the direct evaluation of HFX via the CP2K/QUICKSTEP code are presented.

A. Basis set

The basis set used for this calculation has been specifically constructed for the current purpose, which is an accurate but computationally feasible HF calculation on bulk LiH. The basis constructed here is similar to the polarization consistent (pc) basis sets derived by Jensen.[32–34] Jensen introduced a sequence of quasioptimal basis sets (pc-[0–4]) that rapidly converge to the HF and DFT basis set limit. The pc-3 basis set gives atomization energies with a mean error smaller than 1 kJ/mol. For H and Li the pc-3 basis set has a composition $9s4p2d1f/5s4p2d1f$ and $14s6p2d1f/6s3p2d1f$, respectively, while we adopt $8s3p2d1f/6s3p2d1f$ and $13s6p2d1f/11s5p2d1f$. However, the primitives of the basis employed here are nonstandard and optimized for the present calculations.

In a first step, we have removed primitive Gaussians with exponents smaller than 0.15 bohr^{-2} since diffuse basis functions are technically troublesome. Diffuse functions, which are needed to describe density tails in atoms or molecules, are not needed in the bulk of densely packed solids with large band gaps as the case of LiH. Indeed, we exploit the fact that the basis functions on the lattice sites are available for the expansion of any orbitals, be it the crystal orbitals in the bulk or the atomic orbitals of the isolated atoms. This basis is thus only suited for atomic or surface calculations if ghost basis functions are left in the regular lattice positions to appropriately describe the aforementioned tails of the electron density.

TABLE I. Details for the adopted basis sets for the compositions $8s3p2d1f/6s3p2d1f$ and $13s6p2d1f/11s5p2d1f$ of hydrogen and lithium, respectively. Shown are angular momentum, Gaussian exponent, and corresponding contraction coefficients.

Species	l	Exponent	Coefficient
H	*s*	0.27463675×10^{2}	1.00000000
	s	0.68559258×10^{1}	1.00000000
	s	0.17679972×10^{1}	1.00000000
	s	0.51181842	1.00000000
	s	0.20167548	1.00000000
	s	0.30797000×10^{4}	0.00023473
		0.46152000×10^{3}	0.00182450
		0.10506000×10^{3}	0.00959330
	p	0.21240865×10^{1}	1.00000000
	p	0.10736812×10^{1}	1.00000000
	p	0.56838662	1.00000000
	d	0.92833840	1.00000000
	d	0.49583000	1.00000000
	f	0.12073480×10^{1}	1.00000000
Li	*s*	0.13360341×10^{4}	1.00000000
	s	0.44429982×10^{3}	1.00000000
	s	0.14779702×10^{3}	1.00000000
	s	0.49209451×10^{2}	1.00000000
	s	0.16428957×10^{2}	1.00000000
	s	0.55293994×10^{1}	1.00000000
	s	0.19052824×10^{1}	1.00000000
	s	0.70025874	1.00000000
	s	0.29958682	1.00000000
	s	0.16636288	1.00000000
	s	0.70681000×10^{5}	0.00000544
		0.13594000×10^{5}	0.00003328
		0.31004000×10^{4}	0.00019175
	p	0.15709110	1.00000000
	p	0.74875864	1.00000000
	p	0.38614089	1.00000000
	p	0.22620503	1.00000000
	p	0.28500000×10^{2}	0.00036754
		0.66400000×10^{1}	0.00322359
	d	0.77920820	1.00000000
	d	0.40789925	1.00000000
	f	0.73706300	1.00000000

In a second step, all but the core exponents have been optimized by minimizing the energy of bulk LiH subject to a restraint on the condition number of the overlap matrix. This procedure is similar to the one employed for the molecularly optimized basis sets described in Ref. 35. In CP2K, density functionals that do not include Hartree-Fock exchange can be computed in a highly efficient manner, and in order to make this procedure computationally efficient, such a semilocal density functional [B88 (Ref. 36)] has been employed in the optimization process. The resulting basis is well conditioned, the condition number of the overlap matrix is 2.8×10^4 for bulk LiH. We have estimated the accuracy of the optimized basis by comparing to pc-4-like basis sets, which for this system are only feasible with local DFT, and estimate the total energy of bulk LiH (per unit of LiH) to be well within 0.001 a.u. of the basis set limit, while the basis set error on the cohesive energy is likely smaller than 0.1% (0.0001 a.u.). The details of this optimized basis set are summarized in Table I.

B. Extrapolation of SR-HFX to full range (GAUSSIAN)

All Gaussian calculations presented in this work are based on a very efficient implementation of the SR-HFX energy exploiting a distance-based screening protocol.[31] Using local basis functions it is convenient to express the HFX energy for closed shell as

$$E_x^{\mathrm{HF}} = -\frac{1}{2}\sum_{\mu\nu\gamma\delta} P^{\mu\gamma}P^{\nu\delta}(\mu\nu|\gamma\delta)_g, \tag{1}$$

where $P^{\mu\gamma}$ are density-matrix elements and

$$(\mu\nu|\gamma\delta)_g = \int \mu(\mathbf{r}_1)\nu(\mathbf{r}_1)g(r_{12})\gamma(\mathbf{r}_2)\delta(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \tag{2}$$

are the four-center electron repulsion integrals (ERIs), represented in an atomic-orbital basis. The applied interaction potential $g(r_{12})$ is usually equal to the Coulomb kernel $\frac{1}{r_{12}}$.

For large gap systems, it has been shown that local single-particle wave functions as well as the corresponding density matrix decay like $e^{-h|\mathbf{r}_1-\mathbf{r}_2|}$ for large $|\mathbf{r}_1-\mathbf{r}_2|$, where h is proportional to $\sqrt{E_{\mathrm{gap}}}$, the square root of the band gap of the system of question.[37–40] This is the basic motivation behind SR-HF as, e.g., used in the successful HSE hybrid functional.[12,13] HSE is based on a screened Coulomb interaction $g(r_{12})$ splitting the conventional Coulomb kernel, $\frac{1}{r_{12}}$, into

$$\frac{1}{r_{12}} = \underbrace{\frac{\mathrm{erfc}(\omega r_{12})}{r_{12}}}_{\mathrm{SR}} + \underbrace{\frac{\mathrm{erf}(\omega r_{12})}{r_{12}}}_{\mathrm{LR}}, \tag{3}$$

where the LR and SR parts of the interaction are described by the computationally convenient error function and its complement, respectively. The parameter ω in Eq. (3) determines the extent of the range separation of the Coulomb interaction.

In view of the relatively large HF band gap of LiH (10.8 eV) (Ref. 41) and the fast decay of the density matrix, we will calculate the total HF energy by doing a series of SR-HF calculations at different ω, and extrapolating to $\omega\rightarrow0$. As corroborated by numerical results shown in Sec. III, such an extrapolation of the screened HF energies of the crystal to the full-range HF limit in the specified basis set is numerically robust and reliable.

All calculations are based on a locally modified development version of the GAUSSIAN electronic-structure program.[30] Hence, the total energies presented in Sec. III do not include any DFT contributions. Only Hartree and screened HFX energies are evaluated. The root-mean-square (rms) convergence criterion for the density matrix in the self-consistent-field (SCF) iteration was set to 10^{-7} a.u., which implies an energy convergence no worse than at least 10^{-8} a.u. (GAUSSIAN keyword: SCF=tight). Furthermore, a $24\times24\times24$ mesh of k points was used, which is equivalent to 6912 k points and thus all calculations are sufficiently converged with respect to k points. The large band gap of LiH in the HF approximation (see above) substantially helps converging the k-point integration.

Following ideas found in the literature,[42,43] we apply Padé approximants of various orders to the obtained series of screened HF energies. The actual form of the Padé approximants are the rational polynomials

$$\frac{p(x)}{q(x)} = \frac{\sum_{i=0}^{n} p_i x^i}{\sum_{j=0}^{m} q_j x^j}. \tag{4}$$

Equation (4) represents the general expression of a Padé approximant of order $[n/m]$. Throughout this work only *diagonal* rational polynomials are applied,[42,44] which means that the order of the polynomial in the numerator equals the order of the polynomial in the denominator. Note that the number of parameters to be fitted is $2n+1$ in the case of diagonal polynomials. This is the minimum number of data points, which must be included in the least-squares fit.

For all extrapolations employed in the present work, ω has been chosen to lie in the interval [0.04; 1.0]. In order to put a higher weight to the area near to full-range HF we decided to increment ω by 0.005 up to 0.1 and increment ω by 0.01 up to a value that amounts to 0.2. For the remaining interval of larger ω values, the screening parameter was incremented by 0.1. As a consequence, each fit is based on 31 data points, representing pairs of the screening parameter ω and the corresponding SR-HF energy.

The HF equilibrium lattice constant and bulk modulus have been obtained by fitting the volume dependence of the static lattice energy to the Murnaghan equation of state.[45] The points were chosen in order to cover a range of ±3% around the supposed equilibrium lattice constant of 4.108 Å (seven-points fit).

C. HFX and periodic boundary conditions using Gaussian basis functions

In hybrid functionals, which incorporate a fraction of nonlocal HFX [Eq. (1)], the decay of the Hamiltonian matrix elements (see Sec. II of Ref. 46) with distance is determined by two factors: (i) the decay behavior of the density matrix, $P_{\mu\nu}$, and (ii) the decay behavior of the ERIs. For metallic as well as insulating systems, a screened Coulomb interaction accelerates the convergence of the ERIs in real-space drastically, i.e., the number of replica cells needed for convergence is substantially decreased (see Refs. 47 and 48). Fock exchange calculations involving the long-range tail of the Coulomb interaction [e.g., in the $\omega \to 0$ limit, see Eq. (3), in long-range corrected hybrids or in global hybrids], both the density matrix and the ERIs influence the convergence of the HFX energy.

It is a matter of fact, that due to the algebraic structure of Eq. (1), contributions to the HFX energy can be significant even far from the central cell, precluding an early truncation of the lattice sum (see Eq. 2.4 in Ref. 46). Small exponent basis functions involved in the calculation of the density matrix become important factors determining the computational workload. Calculations under periodic boundary conditions involving SR-HFX with a reasonably large value for the screening parameter ω [Eq. (3)] are tractable for moderately diffuse Gaussian basis functions, i.e., minimal exponent equals ≈ 0.2. Conventional HF or long-range HF calculations are likely to be computationally prohibitive except for high-exponent Gaussian basis sets. The relatively large and diffuse basis set used in this work (see Table I) prevents calculating the HFX at or close to $\omega = 0$, i.e., the long-range limit for this particular system in the given basis. As shown by the results presented in Sec. III, a numerically stable fit to a sufficiently large series of SR-HFX calculations is practicable to calculate an accurate estimate for the HF energy of extended (insulating) systems using large Gaussian basis sets. In summary, $\omega = 0$ is not practical whereas a 31 point ω extrapolation works very well.

D. Direct calculation of HFX (CP2K)

The focus of CP2K is the simulation of complex systems with a variety of methods. Recently, the capability to perform first-principles molecular-dynamics simulation with density functionals including a fraction of Hartree-Fock exchange has been implemented and demonstrated for condensed-phase systems containing a few hundred atoms.[22] With this goal in mind, the implementation is massively parallel, focuses on in-core calculations, uses the Γ point only, and does not exploit molecular or crystal symmetries. The implementation was based on a minimum image convention[49] and employed a standard $1/r$ Coulomb operator. The current implementation, which will be described in detail elsewhere,[50] goes beyond the minimum image convention, and instead employs a truncated Coulomb operator which is defined as

$$g(r_{12}) = \begin{cases} \dfrac{1}{r_{12}}, & r_{12} \le R_c \\ 0, & r_{12} > R_c . \end{cases} \tag{5}$$

This operator was suggested by Spencer and Alavi[51] to obtain rapid convergence for the Hartree-Fock energy with respect to the k-point sampling of the exchange energy in periodic systems. Note that the use of the truncated Coulomb operator implies that the exchange energy is unconditionally convergent for all k points. Furthermore, since exchange in insulators is effective on shorter range compared to the electrostatic interaction, results converge exponentially to the Hartree-Fock limit as R_c is increased. In line with the results presented in Ref. 51, we find that for a cubic cell with edge L and $R_c = L/2$, converged results of the exchange energy can be obtained using the Γ point only. Of course, this requires that the computational cell is sufficiently large so that the Γ-point approximation is acceptable, which in turn requires that the extent of the maximally localized Wannier functions is smaller than $L/2$. Consequently, the exchange energy computed in CP2K is defined as

$$-\frac{1}{2}\sum_{i,j} \int\int \psi_i(r)\psi_j(r) g(|r-r'|)\psi_i(r')\psi_j(r') d^3r d^3r' , \tag{6}$$

where ψ_i are the wave functions at the Γ point. In the Gaussian basis set employed, the exchange energy per cell is thus obtained from

$$-\frac{1}{2}\sum_{\mu\nu\gamma\delta}\sum_{\mathbf{abc}} P^{\mu\gamma}P^{\nu\delta}(\mu\nu^{\mathbf{a}}|\gamma^{\mathbf{b}}\delta^{\mathbf{b+c}})_g , \tag{7}$$

where μ, ν, γ, and δ are the indices of the basis functions in the central cell, and **a**, **b**, and **c** run over all image cells. Due to the rapid decay of the basis functions, sums over image cells **a** and **c** converge quickly. The sum over **b** converges quickly and unconditionally for our choice of $g(r_{12})$. Further technical details, including how to compute efficiently and accurately the required four center integrals $(\mu\nu^{\mathbf{a}}|\gamma^{\mathbf{b}}\delta^{\mathbf{b+c}})_g$ will be presented elsewhere.[50]

III. RESULTS

A. HF energy of LiH at experimental volume using Padé approximants

Figure 1 depicts the obtained series of 31 data points of screened HF energies for various values of $\omega \in [0.040;1.0]$ (see Sec. II) calculated at the experimental lattice parameter. The series of calculated energies clearly converges to a certain limit with decreasing ω. At this point we remind the reader that for the limit $\omega \to 0$ the SR Coulomb kernel given in Eq. (3) approaches the full-range $1/r$ operator. As shown in Fig. 1 and outlined in Sec. II, the density of data points increases significantly toward the $\omega \to 0$ limit. Table II presents results for several least-squares fits obtained using rational polynomials up to order 7. In addition, correlation coefficient r, rms deviation (rmsD) as well as relative rmsD, which is normalized to the range of observed data, i.e., calculated energies, are shown. Since r is very close to 1, we decided to present in Table II $(1-r)$, where a value of zero means perfect agreement between calculated data points and fit.

Apparently, the rmsD as well as relative rmsD values decrease with increasing order of the rational polynomial applied to the fit. Rational polynomials of order 8 or beyond (not shown in Table II) lead to unstable fits and the goodness

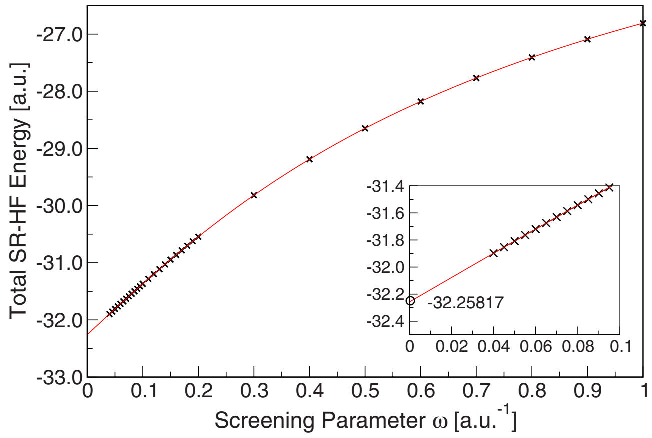

FIG. 1. (Color online) Convergence of the SR-HF energy (a.u.) of a LiH unit cell containing four LiH ion pairs at experimental lattice constant (4.084 Å) with decreasing screening parameter ω involved in the short-range Coulomb interaction. Gaussian results for each ω are represented by crosses. The line shows the [7/7] Padé fit to the numerical data (see text for details). The inset gives SR-HF energies for $\omega \in [0;0.1]$ a.u.$^{-1}$ as well as the extrapolated value for $\omega = 0$ in Hartree atomic units.

of the fit deteriorates. According to Table II the optimal order of the Padé approximant is [7/7], which was used for all extrapolations employed in this work.

As a next step we had to validate the [7/7] polynomial, since it is well known, that algorithms for interpolation are straightforward, whereas for extrapolation care must be taken. A plausible strategy is simply the prediction of energies for a certain value of ω not included in the fit. Table III shows a series of predictions for screened HF energies for a series of ω's starting from $\omega = 0.070$ a.u.$^{-1}$. The corresponding screened HF energy has been estimated based on a [7/7] fit using 24 data points, where $\omega \in [0.075;1.0]$. As can be seen from Table III, it is remarkable that the resulting error is only one order of magnitude larger than the applied SCF convergence criterion (see Sec. II). The error for the predicted energies is practically converged after inclusion of only one further data point and amounts to 3×10^{-7} a.u. Hence, the error incurred by the fit to the Padé approximant is much lower than the convergence threshold in the SCF procedure. By virtue of the aforementioned validations it is safe to give the total HF energy for a unit cell containing four LiH ion pairs at experimental lattice constant (4.084 Å) with a precision of five decimals in Hartree atomic units, which amounts to −32.25817 a.u. The total HF energy per formula unit at experimental lattice constant is given in Table IV and compared with the HF energy obtained using CP2K. Both values agree excellently to significant precision.

TABLE II. Results for the Padé fits to the 31 SR-HF energies (a.u.) of LiH at experimental lattice constant (4.084 Å) for a cell containing four LiH ion pairs. The first column shows the order of the Padé polynomials representing them by the order of the polynomial of the numerator and denominator, respectively (in squared brackets). The extrapolated total HF energy for the cell is given in Hartree atomic units.

Fit	(1-r) [a]	rmsD[b]	rmsD%[c]	E(HF) (a.u.)
[1/1]	6.7×10^{-5}	0.0185955	0.3654035	−32.3526129
[2/2]	5.7×10^{-8}	0.0005666	0.0111347	−32.2472782
[3/3]	5.5×10^{-7}	0.0018244	0.0358500	−32.2521383
[4/4]	2.0×10^{-10}	0.0000364	0.0007156	−32.2585728
[5/5]	7.9×10^{-10}	0.0000759	0.0014909	−32.2588628
[6/6]	1.5×10^{-9}	0.0001109	0.0021803	−32.2576031
[7/7]	6.2×10^{-15}	0.0000002	0.0000046	−32.2581712

[a] r: correlation coefficient (see text for details).

[b] rmsD: root-mean-square deviation.

[c] rmsD%: normalized root-mean-square deviation.

B. HF lattice constant and bulk modulus with GAUSSIAN

Figure 2 shows the seven-points fit of the obtained Padé extrapolated HF energies to the Murnaghan equation of state as outlined in Sec. II B. The rmsD value of this fit amounts to 1.4×10^{-4}. The resulting HF equilibrium lattice constant of LiH equals 4.105 Å and is in excellent agreement with the result obtained by Gillan *et al.* (see Table IV). The corresponding bulk modulus of LiH amounts to 32.34 GPa, which is again in very good agreement (0.9% deviation) with the results obtained by aforementioned workers. Note that bulk moduli are quite sensitive to the equilibrium volume at which they are evaluated and overall good indicators for the quality of the underlying energies at the various volumes.

C. Total and cohesive energy at experimental volume with CP2K

Total energies have been computed for systems of increasing system size by explicitly repeating the cubic unit cell periodically in three dimensions. The largest cell employed is a 5×5×5 repetition of the basic cubic cell and contains exactly 1000 atoms. For this system, 37 500 Gaussian basis functions are used for the expansion of the molecular orbitals, which makes this a computationally demanding simulation. With increasing system size, we also increase the range of the truncated Coulomb operator, in steps of 2 Å up to a maximum of 10 Å (see Table V). The Γ-point approximation therefore converges quickly (exponentially) to the HF limit of this system. We thus obtain from a direct calculation, without extrapolation, an accurate estimate of the total energy per unit cell of approximately −32.258179 a.u. The finite-size error on this result is estimated to be smaller than 50 μE_h. Furthermore, this number is in excellent agreement with the Padé-extrapolated SR-HF results (−32.258171 a.u., Table II), and thus provides numerical evidence for the quality of both approaches. Calculating the HF energy of the H atom and the Li atom with the current basis set, in periodic boundary conditions and retaining the basis functions of all other atoms in the unit cell, we can obtain a consistent estimate of the cohesive energy. In our approach, due to the fact that unrestricted calculations are needed for the atoms, these calculations are even more demanding than the bulk, and have only been performed up to a 4×4×4 repetition of the basis unit cell. Our best estimate for the cohesive energy,

TABLE III. Validation of the [7/7] Padé fit. The first column gives the number of data points (i.e., SR-HF energies) included for a [7/7] Padé fit in order to predict the SR-HF energy corresponding to the ω value given in the second column. Deviations between calculated and fitted SR-HF energies are given in the fifth and sixth column, respectively.

dp	ω	$E^{\text{SR-HF}}$ (a.u.)	E^{fit} (a.u.)	Error	% error
24	0.070	−31.630779	−31.630965	−0.0001817	0.000574
25	0.065	−31.675185	−31.675183	0.0000010	−0.000003
26	0.060	−31.719533	−31.719533	0.0000003	−0.000001
27	0.055	−31.763998	−31.763998	0.0000003	−0.000001
28	0.050	−31.808571	−31.808571	0.0000003	−0.000001
29	0.045	−31.853244	−31.853244	0.0000003	−0.000001
30	0.040	−31.898007	−31.898007	0.0000004	−0.000001

obtained from just three calculations (bulk LiH, and the atoms Li, H) without extrapolation, is −131.949 mE_h. Also here, the finite-size error is estimated to be smaller than 50 μE_h. This number is in excellent agreement with the best estimate obtained by Gillan *et al.*[24] −131.95 mE_h.

It is noteworthy to comment on the calculated HF cohesive energies of LiH obtained using the CRYSTAL code (see Table IV). As already mentioned in Sec. I, an assessment of the HF method implemented in CRYSTAL close to the basis set limit has not been published yet. However, in view of the fact that all cohesive energies of LiH obtained using CRYSTAL are above the correct value, it appears that the Gaussian basis sets used for the cohesive-energy calculations in Refs. 16 and 52 are too restricted to obtain a comparable high level of accuracy to the one pursued in the present work. A comment in Sec. 3.1 of Ref. 16 makes it appear unlikely that calculations close to the HF limit will be feasible using the current CRYSTAL code.

IV. CONCLUSIONS

The Hartree-Fock energy of solid LiH has been calculated using large Gaussian basis sets. Two different approaches, extrapolation of a Padé fit to a series of SR-HFX calculations and direct calculation using a truncated Coulomb operator, have been found to yield total energies that agree to better than 0.1 mE_h. Calculations of the cohesive energy, the equilibrium lattice constant and the bulk modulus agree with the best estimates available in literature. These results show that robust and accurate calculations with nearly converged Gaussian basis sets have now become possible in the condensed phase at least for large band gap systems. However, we reiterate that the computational workload for both methods introduced in the present work is strongly dependent on the decay properties of the density matrix. Thus, for e.g., small gap semiconductors it is very likely that extrapolation of SR-HFX energies to full range would become difficult whereas the truncated Coulomb operator approach will still be robust enough to enable small gap materials being treated on the HF level using large Gaussian basis sets. Certainly, high-accuracy results ask for tailoring high-quality basis sets, as the one introduced in this work. Clearly, finding the optimal Gaussian basis set is certainly nontrivial and the degree of complexity in this task increases with the complexity of the material of interest. Finally, we stress that these results

TABLE IV. Summary of total HF energies per formula unit, HF cohesive energies, equilibrium lattice constants, and bulk moduli of LiH obtained using GAUSSIAN and CP2K. For comparison purpose, results found in the literature are included.

	E(HF) (E_h)	$\varepsilon^{\text{coh}}_{\text{HF}}$ (mE_h)	a_0 (Å)	B (GPa)
GAUSSIAN	−8.064543[a]		4.105	32.34
CP2K	−8.064545[a]	−131.949[a]		
CRYSTAL[b]		−129.14	4.121	28.3
CRYSTAL[c]		−130.16		
VASP[d]		−131.7 [a]		
Gillan *et al.*[e]		−131.95 [a]		
Gillan *et al.*[e]		−131.99	4.108	32.05

[a] Calculated at experimental lattice constant (4.084 Å).
[b] Reference 16.
[c] Reference 52.
[d] Reference 21.
[e] Reference 24.

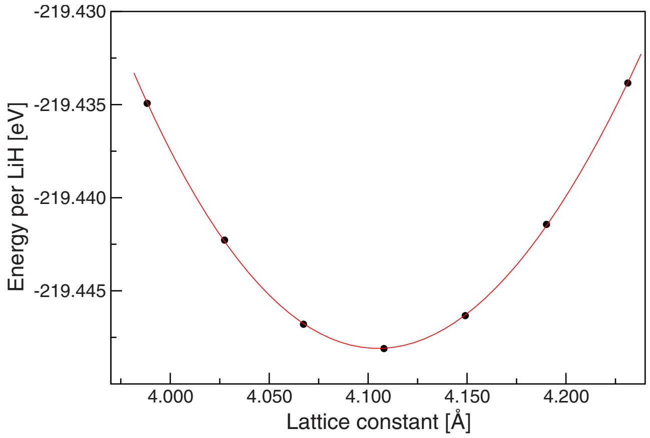

FIG. 2. (Color online) Murnaghan equation of state (red/gray line) for LiH obtained using the HF approximation. Each of the seven points corresponds to the extrapolated least-squares fit of 31 screened HF energies to a Padé approximant of order [7/7] (see text for details).

TABLE V. Results obtained with CP2K and the truncated Coulomb operator for unit cells that are a multiple of the cubic unit cell (4.084 Å). The columns show the size of the unit cell, the range of the truncated Coulomb operator (R_c), the Hartree-Fock energy per four LiH ion pairs, the H atom energy, the Li atom energy, and the cohesive energy ($\varepsilon_{\mathrm{HF}}^{\mathrm{coh}}$), respectively.

	R_c (Å)	E(HF) (a.u.)	H[a] (a.u.)	Li[b] (a.u.)	$\varepsilon_{\mathrm{HF}}^{\mathrm{coh}}$ (a.u.)
2×2×2	4.0	−32.244609	−0.499957	−7.428493	−0.132702
3×3×3	6.0	−32.256844	−0.499974	−7.432137	−0.132100
4×4×4	8.0	−32.258022	−0.499974	−7.432582	−0.131949
5×5×5	10.0	−32.258179	N/A	N/A	N/A

[a] Basis set limit −0.500000.

[b] Basis set limit −7.432727.

will contribute to the growing usefulness of hybrid density functionals for condensed-phase applications and opens, for these systems, the way to accurate calculations based on post-Hartree-Fock methods.

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