Wavefunction-based correlated *ab initio* calculations on crystalline solids

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We present a wavefunction-based approach to correlated *ab initio* calculations on crystalline insulators of infinite extent. It uses the representation of the occupied and the unoccupied (virtual) single-particle states of the infinite solid in terms of Wannier functions. Electron correlation effects are evaluated by considering virtual excitations from a small region in and around the reference cell, keeping the electrons of the rest of the infinite crystal frozen at the Hartree-Fock level. The method is applied to study the ground state properties of the LiH crystal, and is shown to yield rapidly convergent results.

I. INTRODUCTION

Density functional theory (DFT) is a very powerful and elegant approach to many-body systems. Its foundations are based upon the Hohenberg-Kohn (HK) theorem [1] which states that the total energy of the ground-state of a many-particle system in a given external potential can be expressed as a universal functional of its electronic charge density. Thus, within a DFT-based formalism, one avoids constructing the many-body wavefunction of the system, and instead computes directly ground-state properties like the total energy, magnetization, lattice constant etc. from its charge density. However, the exact form of the functional embodied in HK is unknown. Therefore approximations are required, the most important one being the local-density approximation (LDA) developed by Kohn and Sham [2]. LDA has proven to be extremely successful for the ground-state properties of weakly correlated systems. However, for strongly correlated systems such as the ones containing f electrons, its results are far from satisfactory. There have been many improvements proposed to the LDA [3], but their applicability depends on the system involved, i.e., the present DFT-based approaches are not amenable to systematic improvements.

The alternative approach to the problem of electron correlations aims at obtaining the many-particle wavefunction of the system, by approximately solving the corresponding Schrödinger equation within a given one-particle/many-particle basis set. Since the Hamiltonian of the system under consideration is generally known beforehand, there are no uncertainties of principle involved in this approach. One can systematically improve the approach by enlarging the basis set or by including more terms in the expansion of the wavefunction of the system. However, such ”wavefunction-based” approaches scale quite unfavourably with the size of the system. Therefore, in their *ab initio* form, they have been applied mainly in quantum chemistry for small to medium-sized molecules. In condensed-matter physics, wavefunction-based many-body approaches are generally used in conjunction with model Hamiltonians, particularly when the correlations are strong. Usually various approximations have to be made [4] and an extension of *ab initio* quantum-chemistry type of methods to infinite systems did not seem feasible for a long time.

Two recent developments may possibly bring *ab initio* wavefunction-based calculations for infinite systems within the reach of routine computations: (a) advent of more powerful computers (b) use of local excitations in electronic structure calculations. The first of the aforementioned developments is technological in nature, and its importance is self-explanatory. The second development is based on the fact that the correlation hole of an electron is a real-space phenomenon. Local or localized orbitals can immediately tell us as to which electrons will interact with each other strongly, and which ones weakly. Although this has been realized long ago in solid-state theory [5] as well as quantum chemistry [6] only recently have people started following it in full earnest [7–9]. Realizing the potential behind the localized-orbital-based approaches in the electronic structure theory of solids, one of us developed the so-called “incremental scheme” [10]. The incremental scheme is basically an expansion of the total correlation energy per unit cell of a solid written in terms of interactions of increasing complexity among the electrons assigned to localized orbitals (Wannier functions) comprising the solid under consideration. Calculations based upon the incremental scheme have been performed on a variety of solids [11]. However, there is one possible drawback associated with the computations so far, namely, in all correlation calculations the infinite crystal was modelled by a finite cluster. For the ionic systems the cluster was embedded in a Madelung
field, while for the covalent ones the saturation of the dangling bonds with hydrogen was the substitute for the environment.

The purpose of the present work is to study electron correlation effects in a crystalline insulator within the incremental scheme, without compromising on the infinite nature of the system in any way. Thus by comparing the results of the present work with calculations done by the previous cluster-type approximation, we can critically examine both approaches. Bulk LiH was chosen as a first test case for our method. To the best of our knowledge this is the first calculation employing a wavefunction-based approach that does not truncate an infinite solid into a finite cluster. Although the computational efforts involved is more than for the cluster-based calculations, it is not excessive. Therefore, we believe, that with further algorithmic improvements, the present approach can be made viable for solids containing many atoms in a unit cell.

The remainder of the paper is organized as follows. In section II we briefly discuss the theoretical background of the present work. In section III we present the results of our calculations performed on bulk LiH. Finally, in section IV we present our conclusions.

II. THEORY

The starting point of our approach is the representation of the restricted Hartree-Fock (RHF) ground state of the solid in terms of Wannier functions (WFs). It is accomplished by solving the RHF equations of the infinite crystal directly in the Wannier representation, as recently described [12]. The applicability of the approach to periodic insulators of reduced dimensions was demonstrated in another work of ours [13], where we used it to study the ground states of an LiH chain and trans-polyacetylene, at the RHF level. Assuming that the system consists of \( N \) unit cells \( (N \to \infty) \) each of which has \( 2n_e \) electrons, its RHF ground state will be described by \( n_e \) doubly occupied WFs per unit cell. If we use Greek indices \( \alpha, \beta \) etc. to denote the occupied WFs localized in a given unit cell, the RHF wavefunction of a crystal is a Slater determinant composed of Wannier functions \( |\alpha(\mathbf{R}_j); \alpha = 1, n_e; j = 1, N \rangle \). The latter form an orthonormal set

\[
\langle \alpha(\mathbf{R}_j) | \beta(\mathbf{R}_j) \rangle = \delta_{\alpha \beta} \delta_{ij},
\]

and Wannier functions localized in different unit cells are translated copies of each other

\[
|\alpha(\mathbf{R}_i + \mathbf{R}_j) \rangle = \mathcal{T}(\mathbf{R}_j)|\alpha(\mathbf{R}_j)\rangle,
\]

where the operator \( \mathcal{T}(\mathbf{R}_j) \) represents a translation by lattice vector \( \mathbf{R}_j \). LiH has 2 occupied WFs per unit cell. Although, in our approach, the WFs are assumed to be the linear combinations of Gaussian lobe-type functions [14], the theory presented here is quite independent of the choice of the basis set.

The next step is to choose a region of space — henceforth to be called the “correlation region” \( C \) — in which the correlation effects will be computed. The infinite region of space lying outside the correlation region will be called the “environment” \( E \). In the correlation calculations, we consider virtual excitations from the occupied WFs of the correlation region only, keeping the electrons of the environment “frozen” to the occupied (RHF) space. Because of the frozen character of the environment WFs, one can immediately sum up their contribution to obtain an effective one-electron potential called the “environment potential”

\[
U_{pq}^{env} = \sum_{\alpha(\mathbf{R}_j) \in E} (2\langle p\alpha(\mathbf{R}_j) | \frac{1}{\mathcal{T}_{12}} | q\alpha(\mathbf{R}_j) \rangle) - \langle p\alpha(\mathbf{R}_j) | \frac{1}{\mathcal{T}_{12}} | q\alpha(\mathbf{R}_j) \rangle q \rangle,
\]

where \( p \) and \( q \) are two arbitrary basis functions and the factor of two in the first term is due to the spin summation. \( U_{pq}^{env} \) is evaluated using the Ewald summation technique [11], and one is left with an effective Hamiltonian for the electrons located in the region \( C \). The physical interpretation of \( U_{pq}^{env} \) is obvious — it represents the influence of the electrons of \( E \) on those of \( C \).

The correlation contribution to the total energy per unit cell is computed using the aforesaid incremental expansion [10]

\[
\Delta E = \sum_i \epsilon_i + \frac{1}{2} \sum_{i\neq j} \Delta\epsilon_{ij} + \frac{1}{3!} \sum_{i\neq j\neq k} \Delta\epsilon_{ijk} + \ldots,
\]

where the summation over \( i \) involves Wannier functions located in the reference cell, while those over \( j \) and \( k \) include all the Wannier functions of the crystal. The \( \epsilon_i \) (“one-body” increment) are computed by considering virtual excitations only from the \( i \)-th Wannier function, freezing the rest of the solid at the HF level. The “two-body” increment \( \Delta\epsilon_{ij} \) is defined as \( \Delta\epsilon_{ij} = \epsilon_{ij} - \epsilon_i - \epsilon_j \) where \( \epsilon_{ij} \) is the correlation energy of the system obtained by correlating two distinct Wannier functions \( i \) and \( j \). Thus \( \Delta\epsilon_{ij} \) represents the correlation contribution of electrons localized on two “bodies” \( i \) and \( j \). Similarly higher-order increments are defined. For ionic systems such as LiH, generally one- and two-body increments account for the bulk of correlation contribution — three-body increments being negligible. The incremental expansion of Eq. (4) is completely independent of the method of computation. Since LiH is a small system, for the present calculations of increments it was possible to use the full configuration-interaction (CI) approach which in the physics literature is known as the exact diagonalization method. For larger systems, however, full-CI will not be feasible. In that case one can resort to any
of the other available size-extensive correlation schemes \cite{4}.

We finally comment upon the construction of the space of virtual orbitals used to compute the correlation effects. We find it absolutely essential that the virtual orbitals be also localized. For this purpose we adopted the approach suggested by Pulay \cite{18}. It consists of first orthogonalizing the basis functions localized in the reference cell — using projection operators — to the occupied Wannier functions of the reference cell, and to those located in up to third-nearest neighbor unit cells. This yields a set of virtual functions orthogonal to the occupied space, but not orthogonal amongst each other. Orthogonality in the virtual space is finally achieved by a symmetric orthogonalization procedure which does not destroy the local character of the functions. In the end, we obtain virtual Wannier functions which are somewhat delocalized due to their orthogonalization tails, however, quantitatively the delocalization is not very significant. Since occupied and virtual orbitals in our approach form an orthonormal set, almost the whole machinery of electron correlation treatments developed during the last decades in \textit{ab initio} quantum chemistry for atoms and molecules can also be applied to treat polymers or solids.

III. CALCULATIONS AND RESULTS

Among the recent studies of bulk LiH, the most noteworthy are HF level studies of Dovesi et al. \cite{15} and of Bellaïche and Lévy \cite{16}, and DFT-based studies of Bellaïche and coworkers \cite{17,19}. For the sake of comparison, in our study we used the Gaussian lobe representation of the polarized contracted basis sets used by Dovesi et al. \cite{15}, i.e., [3s,1p] on hydrogen and [2s,1p] on lithium. The experimental fcc geometry of the system was assumed with hydrogen on the (0,0,0) position and Li on (0,0,a/2) position, a being the lattice constant. First all-electron Wannier HF calculations were performed at fifteen lattice constants in the range 4.0 — 4.225 Å. The results provided us with the optimized lattice constant and cohesive energy of LiH at the HF level. From the orbitals of these calculations the appropriate environment potentials were constructed (cf. Eq.\eqref{eq:potential}), which were subsequently used to perform incremental-scheme-based correlated calculations, employing the full-CI code of Knowles and Handy \cite{19}. At the correlated level we resorted to the frozen-core approximation by including the Li Wannier functions of region C also in $U^{\text{env}}$. Since Li 1s type orbital is highly localized and core-like, this approximation is quite reasonable and is analogous in spirit to the pseudopotential calculations performed routinely in condensed-matter physics.

In table I we present the results of incremental calculations performed for the infinite solid for the lattice constant of 4.07 Å. The increments reported there include the one-body increment corresponding to the correlation energy of the polarized hydrogen anion of the reference unit cell and the two-body increments involving the interaction of the reference hydrogen anion with those situated in up to third-nearest neighbor unit cells. Note the rapid decrease of the two-body increments with increasing distance between the ions which is of van der Waals type. The reason behind this can be intuitively understood as follows. When, for the purpose of the computation of correlation effects, atoms (or ions) are virtually excited, they develop local (virtual) electric dipole moments. Therefore, the two-body increment corresponds to the interaction of two localized (virtual) dipole moments, the interaction between which is nothing but the van der Waals interaction. A noteworthy point is that localized orbitals are absolutely essential for this argument to hold and, within a Bloch orbital approach, such a simplification is not possible. For the sake of comparison, in table II we also present the results of calculations performed on a finite cluster modelling the bulk LiH, using the same basis set and geometry. The finite cluster calculations were performed with MOLPRO program \cite{20} and include only the most important increments namely one-body and the nearest-neighbor two-body increments. The maximum disagreement of \( \approx 1.6 \times 10^{-3} \) Hartrees between the two calculations is very encouraging, and essentially defines the error bars of the numerics.

The equilibrium lattice constant, cohesive energy and the bulk modulus obtained from our calculations — both at the HF and correlated level — are presented in table I together with results of other authors \cite{21–27}. Before accounting for the zero-point vibrations of the nuclei, the DFT-based calculations systematically underestimate the lattice constant. Since the hydrogen nucleus is very light, one would expect the energy of its zero-point vibrations to make non-negligible contributions to the total energy. Indeed, Roma et al. \cite{27} applying density functional perturbation theory (DFPT) found that the inclusion of the zero-point energy increases the equilibrium lattice constant of LiH by 0.08 Å. Bellaïche et al. \cite{17}, by adding the lattice-constant-dependent zero-point energies obtained by Roma et al. \cite{27}, to their previously derived DFT energies \cite{17} were able to obtain near-perfect agreement with the experimental lattice constant in case of the Wigner expression for the correlation energy, whereas their result is still 0.06 Å too small for the more modern Perdew-Zunger parametrization of the Ceperly-Alder quantum Monte Carlo correlation energy. For the wavefunction-based approaches table I shows that the HF approximation yields a too large lattice constant due to an overestimation of the ionic radii, particularly for the anion. Once electron correlation effects are taken into account, we get an agreement of better than 0.01 Å with the experimental value of the lattice constant, without accounting for zero-point effects.

The experimentally measured cohesive energy of LiH,
corresponding to its dissociation into Li\(^+\) and H\(^-\), is 0.346 a.u. This, when corrected by the difference of the electron affinity of H and the ionization potential of Li, leads to a cohesive energy of 0.176 a.u. with respect to the separation into free Li and H atoms. In the present case, at the correlated level, the Li core is held frozen. Thus the theoretical cohesive energies both at the HF and the correlated level are obtained by subtracting from the total energy per unit cell, the HF limits of the energies of free Li (7.4327 a.u.\(^\text{22}\)) and H (0.5 a.u.) atoms. From table 1 it is obvious that for the HF cohesive energy there is very good agreement among the results of all authors. The difference of 0.0006 a.u. between our results and the one of Dovesi et al.\(^\text{13}\) is possibly due to our use of Gaussian lobe functions instead of Cartesian Gaussians. By subtracting our HF cohesive energy (0.1294 a.u.) from the experimental one (0.1760 a.u.), one gets \(\approx 0.0466\) a.u. as the “experimental” value of the correlation contribution to the cohesive energy per unit cell. The correlated cohesive energy that we obtain in the present work is 0.1644 a.u. and corresponds to 93.4 % of the experimental value. The calculated corresponding correlation contribution of 0.0350 a.u. is 75.1 % of the experimental value.

In order to account for a higher percentage of the correlation contribution we would need to apply larger basis sets including additional diffuse and also higher angular momentum functions. Unfortunately, since our program is still under development, such large-scale calculations are not possible at present. Nevertheless, one can estimate the effect of the basis sets incompleteness for the time being from finite cluster calculations using extended basis sets.\(^\text{29}\) We obtained a value of -0.035486 a.u. for the one-body contribution and -0.001544 a.u. for the nearest-neighbor two-body contributions. Since we are interested in the values of the corresponding contributions obtained with the extended basis sets for the infinite solid within the Wannier function approach, we scale these numbers according to the ratios of the corresponding numbers in the two columns of table 1 and obtain the estimates -0.033652 a.u. and -0.001230 a.u., respectively. By comparing these values to the corresponding numbers obtained with the smaller basis set for the bulk case, we obtain corrections of -0.004335 a.u. and -0.000553 a.u. for the one-body and two-body term, respectively, leading to a total correlation energy gain of -0.0110 a.u. Our so-corrected estimate of the correlation contribution to the cohesive energy per unit cell of 0.0460 a.u. (0.0350 a.u. + 0.0110 a.u.) is in almost perfect agreement with the corresponding experimental number (\(\approx 0.0466\) a.u.).

We want to point out here, that further technical improvements in our implementation of the method will make calculations with extended basis sets for the infinite system feasible and therefore extrapolations from finite cluster calculations unnecessary. The fact that an extension of the basis sets leads to a calculated value essentially in agreement with the experimental result underlines the potential of the proposed method, i.e., the possibility of systematic improvement.

The results of our Wannier-function-based calculations, using the smaller basis set of Dovesi et al.\(^\text{15}\), show that in a sufficiently wide range of values around the equilibrium lattice constant (15 points in the interval 4.0 Å \(\leq a \leq 4.225\) Å) to high accuracy (correlation coefficient 0.999983) the correlation energy depends linearly on the lattice constant \(a\) (\(E_{\text{corr}}(a.u.) = -0.034030 + 0.002935 \times (a(Å) - 4.06))\). This is in agreement with an assumption made in previous work on NiO by Doll et al.\(^\text{14}\). Such a “linear law” is important because it allows one to perform correlated calculations only for two values of the lattice constant near its equilibrium value and to deduce the other values by interpolation. Assuming also a linear behavior of the correlation contributions obtained with the extended basis sets mentioned above, we derive an estimated equilibrium lattice constant of 4.054 Å compared to the actually calculated value of 4.067 Å and the experimental result of 4.060 Å.

Finally, we discuss the influence of correlations on the bulk modulus of LiH. The experimentally measured values reported in literature\(^\text{23, 24}\) are actually obtained by fitting a pressure-volume (\(p(V)\)) relationship to experimental data points. The values for \(\text{^7LiD}\) are only about 1 % to 3 % larger than for \(\text{^7LiH}\)\(^\text{23, 24}\) and sometimes a common value is reported\(^23\). Depending on the chosen ansatz for the \(p(V)\) equation of state (Birch, Murnaghan, Vinet) the values reported for 300 K range from 31.1 GPa to 36.2 GPa, with error bars of 1 % to 6 %. In addition to this uncertainty, the values have to be corrected to 0 K, which roughly corresponds to an increase by 6 % \(^\text{24, 24}\), i.e., a range from 33.0 GPa to 38.4 GPa. A direct comparison of our calculated values, which do not rely on any fitting of an equation of state and are for 0 K, and the effective experimental parameters is to be viewed with care. From table 1 it is obvious that our HF value of 33.4 GPa is in within the interval of experimental values, whereas our correlated (estimated) value of 36.5 (37.9) GPa appears to be slightly too large. Roma et al.\(^\text{27}\) observed a reduction of the bulk modulus by 4 GPa (\(\approx 10\) %) due to zero-point effects. Using their zero-point corrections Bellaïche et al.\(^\text{18}\) were able to obtain close agreement with the experimental values of the bulk modulus in case of the Wigner correlation energy expression (33.9 GPa), whereas for the Perdew-Zunger parametrization also a relatively large value was obtained (36.1 GPa). We note that by adding the corrections calculated by Roma et al.\(^\text{27}\) to our energy-volume data, we end up with correlated results which are not in good agreement with the experimental values, i.e., a lattice constant of 4.143 Å and a bulk modulus of 30.7 GPa. Since our uncorrected values appear to be stable with respect to systematic improvements of the calculation and are also quite close to the experimental values, we believe...
that the zero-point corrections obtained by Roma et al. may be slightly too large, despite the fact that previous estimates were even significantly larger [30].

IV. CONCLUSIONS AND FUTURE DIRECTIONS

In conclusion, a new wavefunction-based approach has been presented, which allows the ab initio determination of electron correlation effects in a crystalline insulator, without abandoning its infinite character. The approach merges ideas from quantum chemistry and solid-state physics, and has the benefit of being amenable to systematic improvements of results. It has been shown to be viable by a first successful application to an ionic crystal, namely bulk LiH. The applicability of the present approach to covalent insulators and semiconductors such as diamond, Si, GaAs etc. is essentially straightforward. The only trivial modification in those cases will be that the occupied (and virtual) single-particle states will consist of bond-centered Wannier functions, instead of the atom-centered Wannier functions encountered in case of ionic systems. As a matter of fact, the viability of the present local approach to electron correlations in covalent systems has already been demonstrated by Paulus et al. [11]—albeit within a finite-cluster approximation—in their study of Group IV semiconductors. Its generalization within the infinite-crystal method presented in this work will be the subject of a future investigation.

As far as the treatment of excited states of crystals is concerned, the quasi-particle excited states such as an electron (hole) in the conduction (valence) band can be treated straightforwardly using the present approach, as these excited states can be regarded as the ground states of \( N + 1 \) \((N - 1)\) electrons, where \(N\) is the total number of electrons in the unperturbed system. Of course, the electron correlation effects in these cases will be more complicated as compared to the \(N\)-particle ground state, owing to the polarization cloud of the extra electron (hole) in the system. Applicability of this approach to quasi-particle excitations was demonstrated by Gräfenstein et al. [31,32], who computed the correlated dispersion relations of holes in the valence bands of Group IV semiconductors. Its generalization to the infinite crystal, as well as extension to the conduction-band dispersion relations, will also be investigated in future.

As far as the general computational viability of our approach is concerned, undoubtedly, at present, it is more demanding than the DFT-based approaches. However, we believe that by utilizing modern order-\(N\) type methods of electronic-structure theory, it can be made competitive with such methods. Conceptually speaking, there is nothing in our approach that restricts its applicability to systems containing unit cells of certain shapes, sizes, or number of electrons. The frontiers in these areas will be decided by the progress in the computer hardware, and by the improvements in the algorithms of electronic structure theory. However, in order to be more specific about the shapes and sizes of the systems which can be studied using the present approach, we believe that more experience with it is essential. Work along these directions is presently underway in our group.

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[1] P. Hohenberg and W. Kohn, Phys. Rev. 136, B 864 (1964).
[2] W. Kohn and L.J. Sham, Phys. Rev. 140, A 1133 (1965).
[3] For a recent review of density-functional-based methods beyond the LDA see, e.g., P. Ziesche, S. Kurth, and J.P. Perdew, Comput. Mat. Sci. 11, 122 (1998).
[4] See, e.g., P. Fulde: Electron Correlations in Molecules and Solids, 3rd edn. Springer Series in Solid-State Sciences, Vol. 100. (Springer, Berlin, 1995).
[5] See, e.g., J. Friedel: The Physics of Metals, ed. by J.H. Ziman (Cambridge University Press, Cambridge 1969).
[6] See, e.g., T. Gilbert in Molecular Orbitals in Chemistry, Physics, and Biology, Ed. P.O. Löwdin and B. Pullman, Academic Press, New York, (1964).
[7] G. Stollhoff and P. Fulde, J. Chem. Phys. 73, 4548 (1980).
[8] P. Pulay, Chem. Phys. Lett. 100, 151 (1983).
[9] C. Hampel and H.-J. Werner, J. Chem. Phys. 104, 6286 (1996).
[10] H. Stoll, Phys. Rev. B 46, 6700 (1992); Chem. Phys. Letters 191, 548 (1992).
[11] See, e.g., B. Paulus, P. Fulde and H. Stoll, Phys. Rev. B 54, 2556 (1996); K. Doll, M. Dolg, P. Fulde, and H. Stoll, Phys. Rev. B 55, 10282 (1997).
[12] A. Shukla, M. Dolg, H.Stoll and P. Fulde, Chem. Phys. Lett. 262, 213 (1996); A. Shukla, M. Dolg, P. Fulde, and H. Stoll, Phys. Rev. B 57, 1471 (1998).
[13] A. Shukla, M. Dolg, and H. Stoll, Phys. Rev. B 58, 4325 (1998).
[14] H. Preuss, Z. Naturf. A 11, 823 (1956); J.L. Whitten, J. Chem. Phys. 39, 349 (1963).
[15] R. Dovesi, C. Ermondi, E. Ferrero, C. Pisani, and C. Roetti, Phys. Rev. B 29, 3591 (1984).
[16] L. Bellaïche and B. Lévy, Phys. Rev. B 54, 1575 (1996).
[17] L. Bellaïche and K. Kunc, Int. J. Quantum Chem. 61, 647 (1997).
[18] L. Bellaïche, J.M. Besson, K. Kunc, and B. Lévy, Phys. Rev. Lett. 80, 5576 (1998).
[19] P.J. Knowles, N.C. Handy, Comput. Phys. Commun. 54, 75 (1989).
[20] MOLPRO is a package of ab initio programs written by H.-J. Werner and P.J. Knowles, with contributions from J. Almlöf, R.D. Amos, M.J.O. Deegan, S.T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, and P.R. Taylor.
[21] J.L. Anderson, J. Nasise, K. Philipson, and F.E. Pretzel, J. Phys. Chem. Solids 31, 613 (1970).
[22] O.L. Anderson, J. Phys. Chem. Solids, 27, 547, (1966).
[23] D.R. Stephens and E.M. Lilley, J. Appl. Phys. 39, 177 (1968).
[24] J.M. Besson, G. Weill, G. Hamel, R.J. Nehmes, J.S. Love-day, and S. Hull, Phys. Rev. B 45, 2613 (1992).
[25] P. Loubeyre, R. Le Toullec, M. Hanfland, L. Ulivi, F. Datchi, and D. Hausermann, Phys. Rev. B 57, 10403 (1998).
[26] D. Gerlich and C.S. Smith, J. Phys. Chem. Solids 35, 1587 (1974).
[27] G. Roma, C.M. Bertroni, and S. Baroni, Solid State Commun. 98, 203 (1996).
[28] E. Clementi and C. Roetti, Atomic Data and Nuclear Data Tables, Vol. 14 (Academic Press, New York, 1974).
[29] The basis set for hydrogen was [6s,5p,4d] and the one for Li was [5s,4p] type. These basis sets are, respectively, referred to as AV5Z and VQZ and were taken from the MOLPRO program library.
[30] J.L. Martins, Phys. Rev. B 41, 7883 (1990).
[31] J. Gräfenstein, H. Stoll, and P. Fulde, Chem. Phys. Lett. 215, 610 (1993).
[32] J. Gräfenstein, H. Stoll, and P. Fulde, Phys. Rev. B 55, 13588 (1997).
TABLE I. Various increments to the correlation energy in Hartrees of bulk LiH computed by the Wannier-function-based approach presented in this work. For comparison, the results obtained using the method of Doll et al. [11] are presented, for the most important increments, under the heading of Finite Cluster. NN stands for nearest neighbors. All the calculations were performed at the lattice constant of 4.07 Å.

| Correlation Increment | Wannier Function | Finite Cluster |
|-----------------------|------------------|----------------|
| one-body              | -0.029317        | -0.030915      |
| two-body (1NN)        | -0.000677        | -0.000850      |
| two-body (2NN)        | -0.000113        | —              |
| two-body (3NN)        | -0.000023        | —              |

TABLE II. Equilibrium values of various quantities for the bulk LiH obtained in this work as compared to those of other authors, and the experiment. Quantities under the column DFT refer to slightly different exchange-correlation functionals used (see Ref. [18] for details). The theoretical results presented below do not include the effect of zero-point vibrations, unless specified otherwise. Lattice constants are in Å, energies in a.u. (i.e., Hartree) and the bulk moduli are in GPa.

| Quantity                  | HF\textsuperscript{a} | HF\textsuperscript{b} | HF\textsuperscript{c} | Correlated\textsuperscript{a} | DFT\textsuperscript{d} | Experiment |
|---------------------------|------------------------|------------------------|------------------------|--------------------------|------------------------|-------------|
| Lattice Constant          | 4.106                  | 4.102                  | 4.110                  | 4.067                    | 3.91–3.98              | 4.060\textsuperscript{f} |
|                           |                        |                        |                        | 3.91–3.98\textsuperscript{f} | 3.99–4.05\textsuperscript{e} |             |
| Cohesive Energy           | 0.1294                 | 0.1302                 | 0.1305                 | 0.1644                   | —                     | 0.1760\textsuperscript{g} |
| Bulk Modulus              | 33.4                   | 34.1                   | 35.0                   | 36.5                     | 33.9–36.1\textsuperscript{e} | 33.0–38.4\textsuperscript{h} |
|                           |                        |                        |                        |                          | 31.3–36.2\textsuperscript{i} |             |

\textsuperscript{a} This work
\textsuperscript{b} Ref. [15]
\textsuperscript{c} Ref. [16]
\textsuperscript{d} Ref. [18], only all-electron results are considered.
\textsuperscript{e} Includes the effect of zero-point motion.
\textsuperscript{f} Extrapolated T=0 value [21]
\textsuperscript{g} The cohesive energy reported here is the “atomic” cohesive energy obtained by correcting the “ionic” cohesive energy reported in ref. [22]. See text for an explanation.
\textsuperscript{h} Estimated for 0 K by scaling 300 K values with 1.06 [24,25,26]
\textsuperscript{i} Estimated for 0 K by scaling 300 K values with 1.06 [24,25,26].