Pressure-Induced Simultaneous Metal-Insulator and Structural-Phase Transitions in LiH: a Quasiparticle Study

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Abstract. – A pressure-induced simultaneous metal-insulator transition (MIT) and structural-phase transformation in lithium hydride with about 1% volume collapse has been predicted by means of the local density approximation (LDA) in conjunction with an all-electron GW approximation method. The LDA wrongly predicts that the MIT occurs before the structural phase transition. As a byproduct, it is shown that only the use of the generalized-gradient approximation together with the zero-point vibration produces an equilibrium lattice parameter, bulk modulus, and an equation of state that are in excellent agreement with experimental results.

Lithium hydride is probably the simplest compound that exists: a strongly ionic crystal with four electrons per unit cell and crystallizing in the rocksalt structure, the so-called B1 phase. Despite this simplicity, LiH and its isotopes are attractive for the study of solid state properties, e.g., electronic structure, lattice vibration, and defect properties. In addition, possible technological applications have motivated extensive studies in the past, as reviewed by Islam [1]. In particular, the metal-insulator transition (MIT) has been studied by several groups [1, 2, 3, 4, 8, 5, 6, 7]. In few alkali hydrides a structural phase transition (PT) from the B1 phase to the B2 (CsCl structure) phase was determined experimentally [1, 7] and theoretically [5, 9, 10] within the local-density approximation. It is only recently that LiH was found to exhibit the same type of PT but at a much higher pressure [10]. Despite this extensive study we believe, as it will be shown later, that this PT is not well understood. The purpose of this Letter is then to present results improving the current understanding of the electronic structure and the MIT in alkali hydrides, using LiH as a prototype. In particular, we address the issue of the pressure-induced MIT by gap closure and structural PT [11], and investigate the different levels of approximations to the total energy, aiming to predict correctly the equilibrium lattice parameter, the bulk modulus, and the equation of state (EoS) of LiH.

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The MITs were classified by Chacham, Zu, and Louie [12] (CZL) as occurring through one of the three following processes: (1) pressure induced structural transformation, (2) magnetic PT of antiferromagnetic insulators, (3) gap closure without phase transformation. For example, xenon and hydrogen are shown by the same authors, using a GW study, to exhibit a pressure-induced MIT of type three [12]. One should remark, therefore, that despite the extensive studies of these kind of PTs within the LDA, they remain poorly described by this theory, because all these types of transitions involve a band-gap closure either directly or indirectly, and it is now well established that the Kohn-Sham density functional theory [13] drastically underestimates the band gap in all types of insulating materials. In this study we will then demonstrate, using a combined total energy calculation and calculated excited states within the GW approximation (GWA), that in LiH the MIT is caused by a PT from the B1 to the B2 phase (transition of type one according to CZL), accompanied by a large band-gap closure and a volume collapse. The LDA incorrectly predicts an electronic MIT within the B1 phase, corresponding to type three PT according to CZL classification, and then under further compression a structural transformation to the B2 phase.

Our Letter is organized as follows. In the first part, we investigate the structural properties of LiH with the all-electron Projector-Augmented-Wave method (PAW) [14]. In order to describe the experimental ground-state properties of LiH, different parameterizations of the exchange-correlation functional have been used. The lattice parameter as well as the EoS are found to be in excellent agreement with experimental data only when the exchange-correlation functional is described within the generalized-gradient approximation (GGA) and the zero-point vibration is included to the total energy. The second part of this work is devoted to the study of excited states using our recently implemented GW approximation [15]. In the last part we address the pressure-induced MIT issue in LiH, and show that it is incorrectly predicted by the LDA.

Electronic Ground State. – Ground-state properties of LiH have been extensively studied in the past [1], mainly in the local-density approximation (LDA). In our case, we use the PAW method, an elegant all-electron method which keeps the simplicity of pseudopotentials but describes correctly the nodal region of the wave functions [14]. In our calculations, the 1s electrons of Li are also included as valence states, since the key role of core electrons has already been pointed out in Ref. [16]. We pay particular attention to the convergence of our calculations(1). The exchange-correlation energy functional has been treated either in the LDA [17] or in the GGA [18]. Fig. 1 presents our calculated ground-state lattice parameter and bulk modulus compared to different calculations [19,20,8,21] and experimental results [22,23].

Our LDA result agrees well with other calculations performed with the same functional, as can be seen in Fig. 1. In our case, a value of 7.39 atomic units (a. u.) is found, but is unsatisfactory compared with experiment [22,23] (about 4.3% smaller). This is not surprising since light atomic masses enhance the volume due to zero-point vibrations (ZPV) of the lattice:

\[ E_{ZP}(V) = \frac{1}{2} \sum_{i,k} \hbar \omega_i(k, V), \]

where \( \omega_i(k, V) \) is the phonon frequency for a wave vector \( k \), branch \( i \) and cell volume \( V \), and are therefore crucial for a proper description of the ground-state properties and the EoS of LiH. In our case, we don’t perform this type of calculation but instead extract the data from Ref. [19]. The addition of the zero-point vibrations (ZPV) improves considerably the

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(1) A mesh of 666 k-points in the full Brillouin zone and an energy cut-off of 100 Ry for the plane-wave basis set have been used.
Fig. 1 – Calculated ground-state lattice parameter \( a \) (in atomic units) and bulk modulus (in GPa) compared with experimental \([22, 23]\) and theoretical \([8, 21, 19]\) results. The labels of the coordinates represent different types of calculations (calculations from 1 to 7 and 12 to 14 use different all-electron methods and 8 and 9 pseudopotentials (PP)). The two vertical dashed lines from left to right represent, respectively, the experimental lattice parameters of Ref. \([22]\) and \([23]\), and the vertical full line the bulk modulus of Ref. \([23]\). The calculations neglecting or including the zero-point vibrations are labeled by NZP or ZPI, respectively. The acronyms CA and Wi stand for the Ceperley-Adler and the Wigner parameterization of the LDA exchange-correlation functional, respectively. We obtain a good agreement with experiment only when both the GGA and the ZPI are included in our calculations.

1. Present work;
2. Ref. \([20]\);
3. Ref. \([8]\);
4. Ref. \([21]\);
5. Ref. \([19]\).

agreement with experiment, but is still insufficient (about 2.3\% smaller). On the other hand, the usage of the GGA as exchange-correlation functional improves the LDA results, but a difference of about 1.8\% remains. A combination of both the GGA and the ZPV are found to be necessary to obtain excellent agreement with the experimental lattice parameter and bulk modulus \([22, 23]\). Therefore the good agreement of Ref. \([20]\) with experiment (see Fig.1) when combining ZPV with Wigner parameterization for the LDA exchange-correlation functional is fortuitous. This is because, as we have shown, the use of the GGA highly improves the LDA results. As a consequence, this agreement cannot be interpreted as a general feature but rather, as mentioned in their work, it is due to a nearly complete cancellation of errors between the exchange and correlation energies when the Wigner parameterization is applied to LiH. The higher LDA value of 7.63 a. u. reported in Ref. \([21]\), which seems closer to the experimental lattice parameter, is in fact due to a poor sampling in the evaluation of Eq. \(1\). Indeed, Roma et al. show that a good sampling leads to a much lower value \([14]\).

Fig. 2 (left plot) presents the equation of state (EoS) for LiH using different type of approximations to the total energy as for the calculation of the lattice parameter. The Birch EoS has been used and the results are compared with experimental data \([24]\). The right plot shows the EoS around the B1-B2 structural transition and will be discussed later. While the LDA results, with or without the phonon contribution, are unsatisfactory, the combination of the GGA and the ZPV leads to an excellent agreement with experiments up to 10\% of compression and to satisfactory agreement for higher compressions.
Excited-states properties. – We studied the excited state properties within the framework of the GW approximation to the selfenergy \[ \Sigma(r, r', \omega) = \frac{i}{2\pi} \int d\omega' G(r, r', \omega + \omega') e^{i\delta \omega'} W(r, r', \omega') \] (3)

where \( G \) is the one-electron Green's function, \( W \) the screened interaction and \( \delta \) a positive infinitesimal. In practice, the quasiparticle energies are obtained using a a Taylor expansion of the selfenergy:

\[
\text{Re} E_n(k) = \epsilon_n(k) + Z_{nk} \times \left[ \langle \Psi_{kn} | \text{Re} \Sigma(r, r', \epsilon_n(k)) | \Psi_{kn} \rangle - \langle \Psi_{kn} | V_{xc}^LDA(r) | \Psi_{kn} \rangle \right]
\] (4)

with

\[
Z_{nk} = [1 - \langle \Psi_{kn} | \frac{\partial}{\partial \omega} \text{Re} \Sigma(r, r', \epsilon_n(k)) | \Psi_{kn} \rangle]^{-1}.
\] (5)

In our case, the screened Coulomb interaction \( W \) is calculated in the random-phase approximation (RPA): no plasmon-pole model is invoked. More details about our implementation are given elsewhere [15]. In Fig 3, the quasiparticle band structure of LiH is presented. The minimum band gap is found to occur at the \( X \) point. The LDA produced an underestimated...
value of 2.64 eV, whereas GW approximation brings it to 4.64 eV, within 7% of the experimental result [20] of 4.99 eV. Others transitions show a considerable improvement compared to experiment (see Table I) [20]. In our calculation, the value of the renormalization factor $Z$ defined in Eq. (5) of $\sim 0.7 - 0.8$ for the valence top band and for the lowest conduction band indicates well defined quasiparticles. A self-interaction correction calculation [8] reported a minimum band gap at the equilibrium lattice parameter of 4.93 eV and of 3.93 eV at 60% compression. In our case, we obtain values of 4.64 eV and 3.97 eV, respectively. It is interesting to notice that the difference is clearly higher at normal pressure. However, it is difficult to reach a general conclusion since the comparison is biased by the use of different methods and basis sets. Moreover, only a simplified SIC scheme has been used in Ref. [8].

Fig. 3 – Calculated LDA (dashed lines) and GW (full lines) electronic band structures of LiH along some high-symmetry directions. The calculation are performed for the B1 phase (NaCl structure) and at the equilibrium volume (lattice parameter = 7.72 a. u.).

Fig. 4 – Pressure evolution of the calculated LDA (dotted lines) and GW (full lines) electronic excitation energies in the B1 phase. Circles and squares represent, respectively, the LDA and the GW calculated points. The dotted and full lines are used as a guide to the eye. The symbol attached to each curve denotes the symmetry of states involved in the electronic transitions. The LDA found, incorrectly, a closure of the band gap before the structural transition takes place, whereas the GW calculations lead to a simultaneous metal-insulator and structural PTs.

The overall agreement of the previous study of the excited states of LiH with experiment is fortuitous and can be traced back to the use of multiple approximations [20]. In particular, (1) the dielectric matrix is computed with a model function, (2) the selfenergy is treated in the core-hole and screened exchange (COHSEX) approximation [20], i.e., the dynamical correlation effects are neglected and finally, (3) the Hartree-Fock wave functions are used as basis set. To compare satisfactorily our calculation with this simplified one, we carried out a calculation with the same COHSEX approximation and showed that, indeed, the neglect of the dynamic correlations leads to larger electronic transition energies than the full GW calculation.

The most interesting point about LiH is the possibility of a pressure-induced MIT. Despite the fact that it is a well studied problem [2,3,4,5,6], it seems that it has never been completely

[20] In order to have well converged results, the GW calculations have been performed using 64 k-points in the full Brillouin zone and a size of the reciprocal-space polarisability matrix of 169 x 169 (See Ref. [15]).
Table I – Comparison of our LDA, COSEX, and GWA electronic transitions and valence bandwidths with others available results. Data in parentheses are results when the denominator of the Green’s function is updated with QP energies.

|        | LDA 1 | COSEX 1 | COSEX 2 | GW Approximation 1 | Expt. 2 |
|--------|-------|---------|---------|--------------------|--------|
| X_{1v} → X_{4′c} | 2.64  | 5.87    | 5.24    | 4.64 (4.84)        | 4.99   |
| L_{2′v} → L_{1c}  | 7.09  | 10.65   | 9.45    | 9.20 (9.53)        | 9.0    |
| X_{1v} → X_{3′c}  | 10.12 | 14.01   | 13.58   | 12.34 (12.64)      | 13.5   |
| Δv = X_{1v} − Γ_{1v}  | 5.35  | 5.71    | 7.16    | 5.15 (5.48)        | 6.3±1.1;6.0±1.5 |
| X_{1v} → X_{4′c}  | 46.10 | 54.59   | 58.82   | 52.43 (53.93)      | 58.4;57.8 |
| X_{1v} → X_{3′c}  | 53.58 | 62.73   | 67.16   | 60.13 (61.73)      | 66     |
| L_{1v} → L_{2′c}  | 56.52 | 65.27   | 70.87   | 62.53 (64.20)      | >72;70.7 |
| L_{1v} → L_{4′c}  | 58.93 | 68.59   | 73.11   | 65.56 (67.24)      | >72;70.7 |

1 Present work; 2 Ref. [26].

solved. Our LDA calculation under pressure (see dotted lines in Fig 4) agrees well with those of Hama et al. [8]. At low pressure the valence and the lowest conduction bands are formed by a bonding and antibonding states of the hydrogen 1s and Lithium 2s states as shown in Fig. 3. At high pressure the bonding anti-bonding band gap becomes larger, and the bottom of the lowest conduction band of lithium 2p character feels a negative pressure and moves towards lower energies, reducing drastically the energy band gap. The closure of the band gap finally occurs at the X high-symmetry point of the B1 phase and the LDA MIT takes place at around 29% of the equilibrium volume [11] a bit lower than the result of Ref. [8]. Nevertheless, the LDA is well known to underestimate energy band gap and therefore to underestimate the volume compression of the MIT. This motivated us to apply our GW method to make a more rigorous study of this PT. In this case (see full lines in Fig 4), the metallic transition is found to occur at 23% of the equilibrium volume, well below our LDA value. The scenario of the band gap closure remains the same as in the LDA. In term of pressure, this brings us to a value of 580 GPa. The disagreement with previous reported results can be traced back to the use of the LDA instead of the GWA. Hama et al. [8] predicted a band gap closure at 226 GPa, and Kondo and Asaumi [6] used first-order Murnaghan EoS to find a metallisation pressure of 400 GPa. However this electronic pressure is irrelevant, since this metallic transition competes with a structural PT from the B1 semiconducting phase to the B2 metallic phase at much lower pressure. This structural transition was not considered by Kondo and Asaumi [5] and by Hama et al. [8] but was studied later by Ahuja et al. [10]. In our case, we have found this structural transition at about 29% of the experimental equilibrium volume; Ahuja et al. [10] found it at about 33%. At this volume, the band-gap closure is already obtained within the LDA, whereas GW still predicts an insulating state. As both LDA and GW calculations predict LiH to be a metal in the B2 phase, at the structural transition volume, the MIT is induced by a structural change and is of type one according to BZL classification [12]. We have found that the PT is accompanied by a volume collapse of 1.2% and a band-gap closure of more than 1 eV [11]. This PT can be achieved experimentally since an experimental pressure of the order of 332 GPa is nowadays within reach.

Conclusion. – In this Letter, lithium hydride has been revisited in many different aspects. We have shown that both the gradient correction and the zero-point motion are crucial for the correct description of the ground state of LiH. We have also shown that the knowledge
of the quasiparticle band structure under pressure is crucial for the prediction of the MIT. In particular, we have pointed out to the importance of applying the GW calculation to LiH by showing, for the first time, that the MIT happen simultaneously with a structural PT. The LDA predicted firstly the MIT and then under further compression the structural transformation. We hope that our work will stimulate further experimental studies of the MIT in LiH.

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