

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 (from the B1 to B2 phase) in lithium hydride with about 1.3% volume collapse has been predicted by means of the generalized-gradient approximation (GGA) in conjunction with an all-electron GW approximation method. The local-density approximation (LDA) wrongly predicts that the MIT occurs before the structural phase transition, whereas the GGA predicts the correct transition but with a very small band gap of the B1 phase at the transition. It is also shown that only the use of the GGA together with the zero-point vibration produces an equilibrium lattice parameter, bulk modulus, and an equation of state that are in excellent agreement with experiment.

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 [1–8]. 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 [8–10] within the local-density approximation. It has been only recently that LiH was found to exhibit the same type of PT but at a much higher pressure [9]. Despite this extensive study, we believe, as 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 at predicting correctly the equilibrium lattice parameter, the bulk modulus, and the equation of state (EoS) of LiH.

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 kinds 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. On the other hand, the GGA produced the correct phase transition, but at the transition the band gap of the B1 phase is too small in agreement with Wang, Ahuja and Johansson [9].

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 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). We use the PAW method, an elegant all-electron method which keeps the simplicity of pseudopotentials but correctly describes 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]. Figure 1 presents our calculated ground-state lattice parameter and bulk modulus compared to different calculations [8, 19–21] 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; nevertheless, our value of 7.39 atomic units (a.u.) 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:

$$E_{\text{ZP}}(V) = \frac{1}{2} \sum_{i,\mathbf{k}} \hbar\omega_i(\mathbf{k}, V), \quad (1)$$

⁽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.

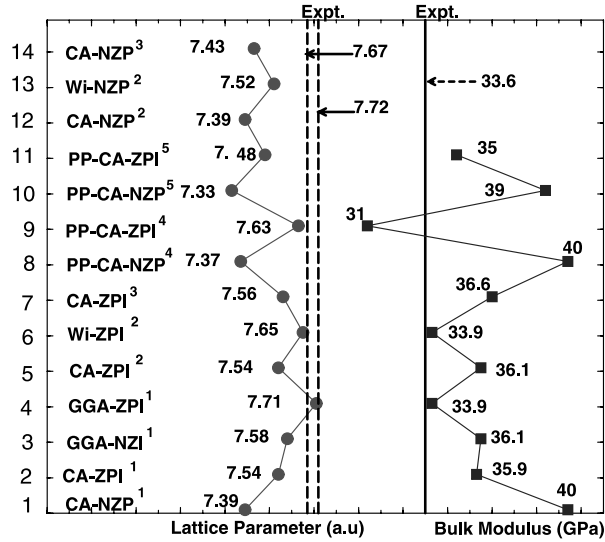


Fig. 1 – Calculated ground-state lattice parameter a (in atomic units) and bulk modulus (in GPa) compared with experimental [22, 23] and theoretical [8, 19, 21] results. The labels of the coordinates represent different types of calculations (calculations from 1 to 7 and 12 to 14 use different all-electron methods and 8 and 9 pseudopotentials (PP)). The two vertical dashed lines from left to right represent, respectively, the experimental lattice parameters of refs. [22, 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. Upper indices are as follows: 1 present work; 2 ref. [20]; 3 ref. [8]; 4 ref. [21]; 5 ref. [19].

where $\omega_i(\mathbf{k}, V)$ is the phonon frequency for a wave vector \mathbf{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 do not perform this type of calculation, but instead extract the data from ref. [19]. The addition of the zero-point vibrations (ZPV) improves considerably the 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 is 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 [19].

Figure 2 (left plot) presents the equation of state (EoS) for LiH using different types 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 in the vicinity of the B1-B2 PT and will be discussed later. While the LDA

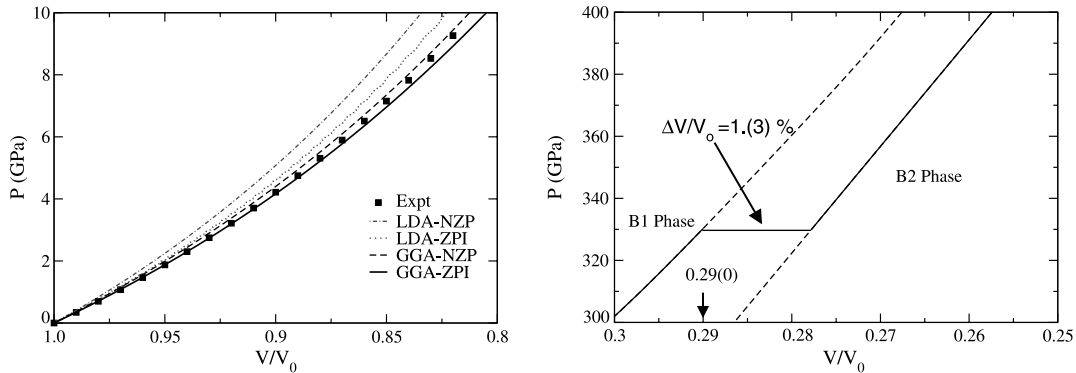


Fig. 2 – The left plot shows the comparison between our calculated Birch EoS, using different types of approximations to the total energy, with experimental results (squares) of ref. [24]. The EoS within the GGA, including the zero-point motion, agrees perfectly with experiment below 0.9 volume compression. The right figure presents the EoS for the two different structural phases at high compressions where the metal-insulator and the structural PTs occur (denoted by a vertical arrow). The $\Delta V/V_0$ value represents a 1.3% volume collapse.

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 self-energy [25]. The purpose of the GWA method is to provide a rigorous formulation for the quasiparticle properties based on Green's func-

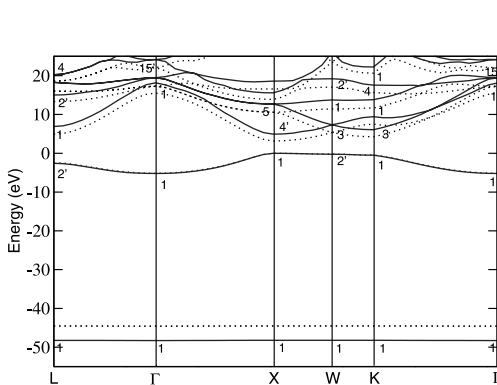


Fig. 3

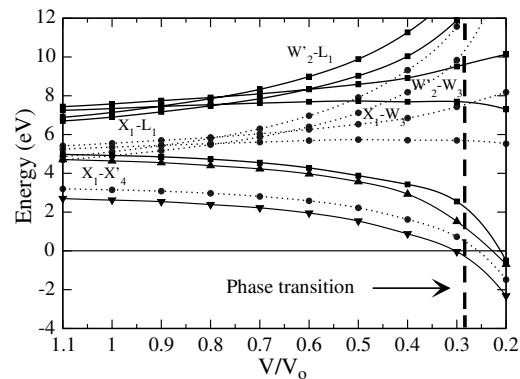


Fig. 4

Fig. 3 – Calculated GGA (dashed lines) and GW-GGA (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 variation of the GGA (dotted lines with filled circles) and GW-GGA (full lines with squares) electronic excitation energies in the B1 phase. For comparison we added the smallest gap within the LDA and the GW-LDA (lines with triangles). The LDA found, incorrectly, a closure of the band gap before the structural transition takes place, whereas the GW-LDA, GW-GGA and GGA calculations lead to a simultaneous metal-insulator and structural PTs.

TABLE I – Comparison of our LDA, GGA, COHSEX, GWA-LDA and GWA-GGA electronic transitions and valence bandwidths with other available results.

	LDA ^a	GGA ^a	COHSEX ^a	COHSEX ^b	GW-LDA ^a	GW-GGA ^a	Expt. ^b
$X_{1v} \rightarrow X_{4'c}$	2.64	3.16	5.87	5.24	4.64	4.92	4.99
$L_{2'v} \rightarrow L_{1c}$	7.09	7.34	10.65	9.45	9.20	9.49	9.0
$X_{1v} \rightarrow X_{5'c}$	10.12	10.59	14.01	13.58	12.34	12.72	13.5
$\Delta_v = X_{1v} - \Gamma_{1v}$	5.35	5.16	5.71	7.16	5.15	5.21	$6.3 \pm 1.1; 6.0 \pm 1.5$
$X_{1v}^{\text{core}} \rightarrow X_{4'c}$	46.10	47.68	54.59	58.82	52.43	53.14	58.4;57.8
$X_{1v}^{\text{core}} \rightarrow X_{5'c}$	53.58	55.12	62.73	67.16	60.13	60.94	66
$L_{1v}^{\text{core}} \rightarrow L_{2'c}$	56.52	57.85	65.27	70.87	62.53	63.27	> 72;70.7
$L_{1v}^{\text{core}} \rightarrow L_{4c}$	58.93	60.55	68.59	73.11	65.56	66.52	> 72;70.7

^a Present work; ^b ref. [26].

tion approach. Briefly, the quasiparticle (QP) energies $E_n(\mathbf{k})$ and wave function $\psi_{\mathbf{k}n}(\mathbf{r})$ are determined from the solution of the QP equation,

$$(T + V_{\text{ext}} + V_{\text{h}})\psi_{\mathbf{k}n}(\mathbf{r}) + \int d^3r' \Sigma(\mathbf{r}, \mathbf{r}', E_n(\mathbf{k}))\psi_{\mathbf{k}n}(\mathbf{r}') = E_n(\mathbf{k})\psi_{\mathbf{k}n}(\mathbf{r}), \quad (2)$$

where T is the kinetic energy operator, V_{ext} the external potential due to the ion cores, V_{H} the average electrostatic (Hartree) potential, and Σ the electron self-energy operator, written in the GW approximation as

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' G(\mathbf{r}, \mathbf{r}', \omega + \omega') e^{i\delta\omega'} W(\mathbf{r}, \mathbf{r}', \omega'), \quad (3)$$

where G is the one-electron Green's function, W the screened interaction and δ a positive infinitesimal. In practice, the quasiparticle energies are obtained using a Taylor expansion of the self-energy:

$$\text{Re } E_n(\mathbf{k}) = \epsilon_n(\mathbf{k}) + Z_{n\mathbf{k}} \times [\langle \Psi_{\mathbf{k}n} | \text{Re } \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_n(\mathbf{k})) | \Psi_{\mathbf{k}n} \rangle - \langle \Psi_{\mathbf{k}n} | V_{xc}^{\text{LDA}}(r) | \Psi_{\mathbf{k}n} \rangle] \quad (4)$$

with

$$Z_{n\mathbf{k}} = \left[1 - \langle \Psi_{\mathbf{k}n} | \frac{\partial}{\partial \omega} \text{Re } \Sigma(\mathbf{r}, \mathbf{r}', \epsilon_n(\mathbf{k})) | \Psi_{\mathbf{k}n} \rangle \right]^{-1}. \quad (5)$$

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⁽²⁾. The minimum band gap is found to occur at the X point. Both the LDA and the GGA produced underestimated values of 2.64 eV and 3.16 eV, respectively, whereas GW approximation brings them to 4.64 eV and 4.92 eV, within less than 2% of the experimental result [26]. Others transitions show a considerable improvement compared to experiment (see table I). A self-interaction correction (SIC) calculation [8] reported a minimum band gap at the equilibrium lattice parameter of 4.93 eV and of 3.93 eV at 60% compression. Our GW-GGA values are 4.92 eV and 4.26 eV, respectively, whereas the GW-LDA produced 4.46 and 3.92 eV. It is difficult to compare the numbers because the methods used are conceptually different. Moreover, only a simplified SIC scheme has been used [8].

⁽²⁾In order to have well-converged results, the GW calculations have been performed using 64 \mathbf{k} -points in the full Brillouin zone and a size of the reciprocal-space polarizability matrix of 169×169 (see ref. [15]).

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 [26]. In particular, 1) the dielectric matrix is computed with a model function, 2) the self-energy is treated in the core-hole and screened exchange (COHSEX) approximation [25], *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 [2–6, 8], it seems that it has never been completely solved. Our LDA calculation under pressure (see down-triangles 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 bonding and antibonding states of the hydrogen $1s$ and lithium $2s$ states, as shown in fig. 3. At high pressure the bonding-antibonding 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, drastically reducing 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 the energy band gaps and therefore to underestimate the compression volume 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 GW-LDA 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 previously 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 [6] and by Hama *et al.* [8], but was studied later by Ahuja *et al.* [9]. In our case, we have found this structural transition at about 29% of the experimental equilibrium volume; Ahuja *et al.* [9] found it at about 33%. At this volume, the band gap closure is already obtained within the LDA, whereas the GW-LDA and the GW-GGA still predict an insulating state (1.2 and 2.25 eV, respectively) As the LDA, the GGA and the 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.(3)% and a band gap closure of 2.25 eV (GW-GGA) [11]. This PT can be achieved experimentally since an experimental pressure of the order of 329 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 the importance of applying the GW calculation to LiH by showing that the MIT happen simultaneously with a structural PT with a large band gap and volume collapse. The GW based on GGA produces band gaps that are in better agreement with experiment than those obtained with the GW based on LDA. On the other hand, the LDA predicted firstly the MIT and then under further compression the structural transformation

and the GGA predicts the simultaneous MIT and structural PT, but unfortunately it shows a continuous decrease of the band gap that almost vanishes at the transition, in agreement with the results of ref. [9]. Thus, a quasiparticle study is required for a good understanding of a combined MIT and structural PT under pressure.

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