Metallization of Molecular Hydrogen: Predictions from Exact-Exchange Calculations

Martin Städele and Richard M. Martin
Department of Physics, University of Illinois at Urbana-Champaign, Illinois 61801
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We study metallization of molecular hydrogen under pressure using exact-exchange (EXX) Kohn-Sham density-functional theory in order to avoid well-known underestimates of band gaps associated with standard local-density or generalized-gradient approximations. Compared with the standard methods, the EXX approach leads to considerably (1–2 eV) higher gaps and significant changes in the relative energies of different structures. Metallization is predicted to occur at a density of $\gtrsim 0.6$ mol/cm^3 (corresponding to a pressure of $\gtrsim 400$ GPa), consistent with all previous measurements.

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Despite great efforts starting with the first theoretical predictions in 1935 [1], the determination of the electronic and structural properties of hydrogen at high pressure is still incomplete [2]. Experimentally, it is established that hydrogen transforms to high-pressure phases, but remains molecular up to pressures of at least ≈ 200 GPa [3]. Metallization of solid hydrogen has been actively sought, but not yet observed, with one experimental team reporting no sign of metallization up to 342 GPa [4]. It is widely assumed that metallization would occur either through a structural transformation to an atomic metallic phase, which involves dissociation of the H_2 molecules, or through band overlap within the molecular phase itself. This latter mechanism is supported by a recent experiment-based equation of state [5] that, combined with quantum Monte Carlo (QMC) calculations for metallic atomic hydrogen [6], yields an estimate for the dissociation pressure of as much as 620 GPa [5].

The theoretical situation is complicated by the fact that the structures at high pressures are not known, together with the well-known difficulties of quantitative predictions for metal-insulator transitions. Various candidate structures for the high-pressure phases (called "phase II" or "BSP" below ≈ 150 GPa and "phase III" or "HA" above ≈ 150 GPa) have been proposed based on static [7–15], and dynamic [16–18] density-functional calculations and on QMC [6] investigations. Most of these structures have hexagonal and orthorhombic unit cells with up to four molecules. However, there are serious difficulties associated with the estimates of metallization pressures. The major problem is the well-known fact that the local-density (LDA) or generalized-gradient (GGA) approximations of density-functional theory cause drastic underestimates of band gaps (by typically 50%–100%). This leads to much too low metallization pressures and also affects the quality of LDA and GGA total energies that are needed for the prediction of energetically favorable structures. Previous work beyond the LDA and GGA was carried out within Slater's Xα approximation to the Hartree-Fock method [11], the many-body *GW* framework in a first-principles [19] and an approximate [15] formulation, and QMC simulations [6]. The first two studies were limited to a simple hcp structure with two molecules per cell oriented along the c axis (called "mhcp" hereafter), which has been found to be energetically unfavorable [7–10]; the *GW* calculations [15,19] are not able to determine relative energies of structures. The QMC calculations indicated qualitatively the problems with the LDA calculations but did not determine gaps.

In this Letter, we present a first-principles investigation of band-gap closure within the molecular phase. We employ the framework of exact-exchange (EXX) density-functional theory, which has been shown recently to yield very accurate band gaps *and* total energies for a large set of semiconductors [20] and to lead to qualitatively correct excitation spectra for molecules [21]. The EXX method has crucial advantages for the present study. Since it treats *exactly* all exchange-related quantities of Kohn-Sham density-functional theory [22], it is inherently self-interaction-free. This remedies largely the band-gap underestimates that plague all LDA and GGA calculations, without an artificial band-gap correction and in a parameter-free way. Second, it yields band structures and total energies *from the same calculation*, which we believe to be a key requirement for the solution of the hydrogen problem.

In the EXX scheme, which is explained in detail in Ref. [20], total energies E_{tot} are obtained from the expression

$$E_{\text{tot}} = T_0 + E_{\text{el-prot}} + E_H + E_x + E_c\,. \tag{1}$$

Here T_0 is the noninteracting kinetic energy, $E_{\text{el-prot}}$ is the interaction energy between the electrons and the protons, E_H is the Hartree energy, E_x the exact exchange energy, and E_c denotes the correlation energy, which is the only quantity that has to be approximated (the LDA is used in this work). Band structures $\{\varepsilon_{n\mathbf{k}}\}$ and wave functions $\phi_{n\mathbf{k}}$ for states with band index n and wave vector $\mathbf{k}$ are obtained from the Kohn-Sham equations

$$\left(-\frac{\nabla^2}{2} + V_{\text{prot}}(\mathbf{r}) + V_H(\mathbf{r}) + V_x(\mathbf{r}) + V_c(\mathbf{r})\right)\phi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\phi_{n\mathbf{k}}(\mathbf{r})\,, \tag{2}$$

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where $V_{\mathrm{prot}}(\mathbf{r})$ is the potential due to the protons, $V_H(\mathbf{r})$ is the Hartree potential, and $V_c(\mathbf{r}) = \delta E_c/\delta n(\mathbf{r})$ with the density $n(\mathbf{r}) = 2\sum_{n\mathbf{k}}^{\mathrm{occ}} |\phi_{n\mathbf{k}}(\mathbf{r})|^2$. The crucial part of the EXX scheme is the construction of the exact local exchange potential $V_x(\mathbf{r}) = \delta E_x/\delta n(\mathbf{r})$ as the functional derivative of the exact exchange energy with respect to the density [20]. Since this requires repeated computation of nonlocal exchange integrals and a linear-response function, an EXX calculation is much more demanding than standard LDA or GGA methods. The present calculations were performed using the bare proton potential for hydrogen and plane-wave basis sets with a kinetic energy cutoff of 36 Ry that has been employed in previous calculations on H_2 [11,12]. We have also performed tests with cutoff energies of 60 Ry and observed that band gaps $\varepsilon_{\mathrm{gap}}$ and total-energy differences ΔE_{tot} among different structures were changed by only a few hundredths of an eV and a few tenths of a mRy/molecule, respectively. Dense $\mathbf{k}$-point meshes with $N_{\mathbf{k}} \approx 3500/N_{\mathrm{at}}$ special points in the Brillouin zone were employed (N_{at} denotes the number of protons in the unit cell). This guarantees convergence of ΔE_{tot} better than 1 mRy/molecule.

First we show how the EXX band gaps compare with LDA and *GW* band gaps over a wide range of densities, as depicted in Fig. 1 for the mhcp structure with the bond length and c/a ratio fixed at the values determined from LDA and extrapolations of x-ray data [19] (the only case for which first-principles *GW* calculations have been done). We can recognize several salient features: (i) EXX gaps are about 1.5–2 eV larger than the LDA gaps for all densities. Consequently, the EXX metallization density is considerably higher than for LDA. (ii) EXX and LDA gaps are almost linear functions of density, which holds also for the gaps of the other structures considered below. (iii) a linear extrapolation of the EXX data to zero density (isolated H_2 molecules) yields a gap of 11.4 eV, close to the weighted average of the lowest experimental singlet and triplet excitation energies of the H_2 molecule [23], 11.6 eV (indicated by the left cross in Fig. 1).

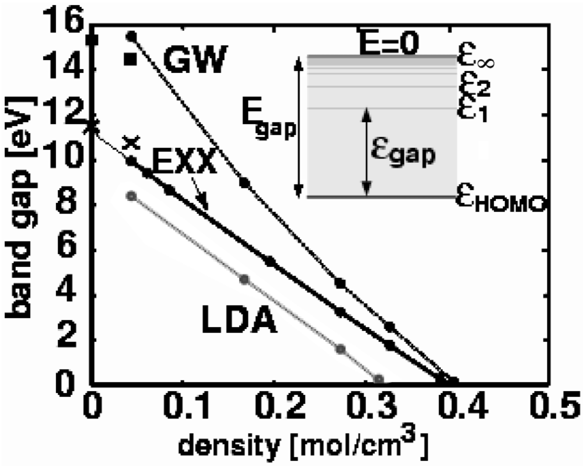

FIG. 1. Fundamental band gaps of the mhcp structure, calculated by the EXX, *GW* [19], and LDA methods. The squares represent experimental estimates for the band gap [32], the crosses denote lowest experimental excitation energies [23,32]. The inset shows qualitatively the EXX eigenvalue spectrum in the zero-density limit.

The last point is in agreement with recent work on isolated noble-gas atoms [24]: the differences between the highest occupied eigenvalue and the unoccupied EXX Kohn-Sham eigenvalues are very good approximations to excitation energies. This can be attributed to (i) the correct asymptotic $-1/r$ behavior of the exact-exchange potential $V_x(\mathbf{r})$ in Eq. (2), which causes the EXX spectrum of the unoccupied states to be a Rydberg series (with energies $\varepsilon_1 < \varepsilon_2 < \cdots < \varepsilon_\infty = 0$, see inset of Fig. 1) and (ii) $\varepsilon_\infty - \varepsilon_{\mathrm{HOMO}}$ equaling the ionization energy I [25]. Indeed, we find $\varepsilon_1 - \varepsilon_{\mathrm{HOMO}}$ in EXX to agree very well with the lowest experimental excitation energies (crosses in Fig. 1), both for the isolated hydrogen molecule and the molecular solid at low density. Thus, the quasiparticle band gap E_{gap}, defined as the difference of the ionization energy and the electron affinity [25], $E_{\mathrm{gap}} = I_{\mathrm{H}_2} - A_{\mathrm{H}_2} \approx I_{\mathrm{H}_2}$, differs from the lowest EXX gap by an exciton binding energy $\varepsilon_\infty - \varepsilon_1$ [26]. At high densities excitonic effects are reduced, so that we expect the real quasiparticle gaps to deviate only slightly from the EXX gaps, just as has been demonstrated for semiconductors [20,27].

For densities greater than 0.35 mol/cm^3, we have also carried out EXX calculations on other structures with hexagonal and orthorhombic unit cells (see Fig. 2) that

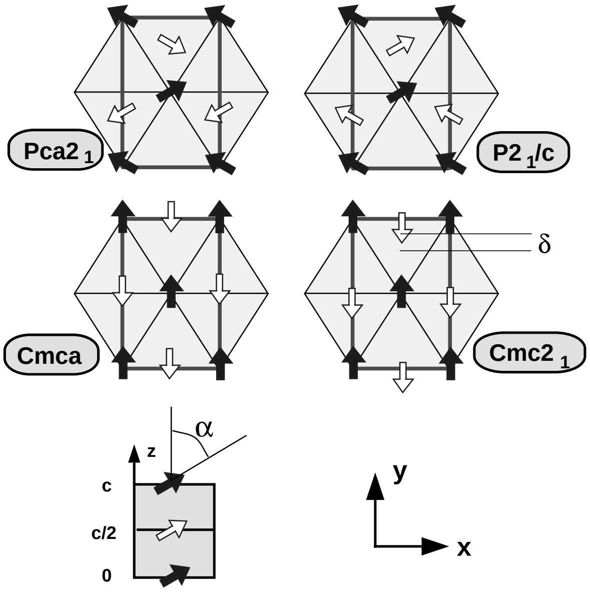

FIG. 2. Possible ground-state structures for solid H_2 at high pressures, projected onto the *xy* plane. Full (empty) arrows represent molecules centered on the *c* (*c*/2) plane and pointing towards the positive-*z* hemisphere. Though some of the structures have a two-molecule minimum basis, we have indicated the rectangular cross sections of orthorhombic four-molecule unit cells for the ease of comparison.

have been proposed previously [7–9] as possible lowest-energy structures on the basis of LDA and GGA total-energy calculations. Here the H_2 molecules are tilted with respect to the z direction by an angle $\alpha \approx 55°$ and the c/a ratio is approximately 1.58 (at high pressures). In the structures denoted by $Cmc2_1^\delta$, the centers of the molecules are displaced from ideal hcp sites by a distance δ (we normalize δ such that $Cmc2_1^1$ coincides with the $Cmca$ structure). Proton coordinates derived from LDA calculations for these structures [7,14] were used as input for the present EXX calculations since a complete unit-cell relaxation within the EXX scheme is computationally too demanding at present.

Figure 3 depicts the fundamental EXX band gaps of the structures of Fig. 2 for densities between $n_1 = 0.35$ and $n_2 = 0.60\ \mathrm{mol/cm^3}$. [The corresponding pressures can be specified by our theoretical calculations or by using an extrapolated experimental equation of state [5,28,29]. We find that at the densities n_1 and n_2, the theoretical pressures (P_1 and P_2) are close to those of Ref. [28], corresponding to 100 and 400 GPa; Ref. [5] leads to much lower pressures at high density ($P_1 = 100$ GPa, $P_2 = 325$ GPa), whereas Ref. [29] gives higher pressures ($P_1 = 115$ and $P_2 = 500$ GPa).] For the $Cmc2_1^{0.5}$, $Pca2_1$, $Cmc2_1^0$, and $P2_1/c$ structures, we obtain metallization densities of 0.468, 0.535, 0.537, and 0.542 $\mathrm{mol/cm^3}$, respectively. Note that the use of LDA coordinates means at high pressure a bond length of $r_0 \approx 1.45$ a.u. We have verified that using the experimental ($r_0^{\mathrm{Expt.}} = 1.40$ a.u.) or EXX ($r_0^{\mathrm{EXX}} \approx 1.38$ a.u.) bond length of the isolated H_2 molecule [30] increases calculated band gaps by about 0.6 and 0.9 eV, respectively. For the $P2_1/c$ structure, this is indicated by the thin dashed lines in Fig. 3. The larger bond length causes the predicted metallization density to increase up to 0.58 $\mathrm{mol/cm^3}$, corresponding to a calculated pressure of 375 GPa.

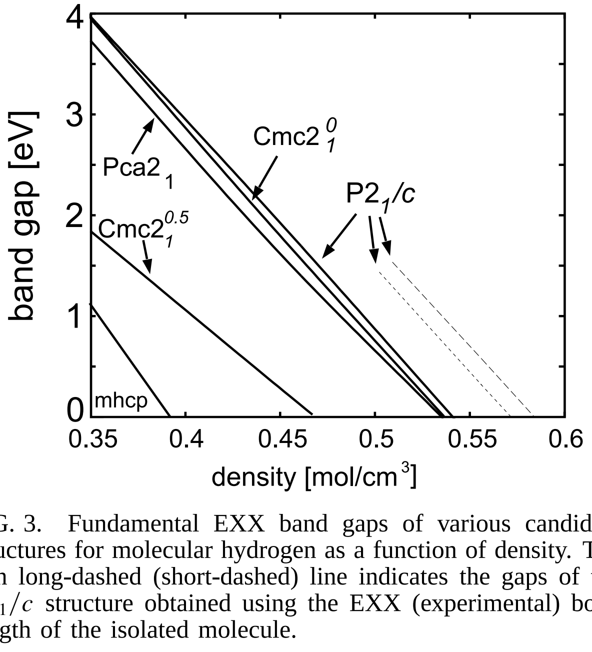

FIG. 3. Fundamental EXX band gaps of various candidate structures for molecular hydrogen as a function of density. The thin long-dashed (short-dashed) line indicates the gaps of the $P2_1/c$ structure obtained using the EXX (experimental) bond length of the isolated molecule.

The EXX scheme predicts that the three structures with the largest gaps ($P2_1/c$, $Cmc2_1^0$, and $Pca2_1$) are the most stable ones, as reported in Fig. 4. A key result of the utilization of the EXX functional is that the metallic $Cmca$ structure becomes more stable than the insulating phases only above a density of 0.61 $\mathrm{mol/cm^3}$ (calculated pressure 415 GPa). In contrast, LDA [15] and GGA calculations [16] find this to be the most stable structure at much lower density (at quoted pressures of $P \approx 140$ and 180 GPa). Such a low metallization pressure is in severe disagreement with experiment, and we believe the problem is a consequence of the erroneous LDA and GGA band gaps that indirectly affect the total energy. The energy is decreased by populating the conduction states, an effect that occurs in the EXX calculations only upon much higher compression. However, the rule "the lower the energy, the wider the band gap" [9] is not exactly obeyed: the most stable structure $Pca2_1$ has only the third highest band gap. We find $Pca2_1$ to be more stable than $P2_1/c$ for all densities, in agreement with the LDA results of Ref. [10], but in disagreement with the LDA and GGA calculations of Refs. [15] and [16] that slightly favor $P2_1/c$.

Zero-point motion of the protons is a very difficult problem that has been the subject of much debate. For the present purposes there are three effects. First, the pressure is increased (by approximately 10% [6]). Second, the band gaps may change. The three most stable structures have gaps that differ only by a few tenths of an eV. One might interpret this as an estimate of the influence of zero-point motion which is expected to average over low-energy structures. Tight-binding calculations on large cells with hydrogen molecules in disordered arrangements [31] indicate effects that are similarly small. However, as the gaps become small, of order of the vibron energies ≈0.5 eV, we expect the zero-point motion to increase the

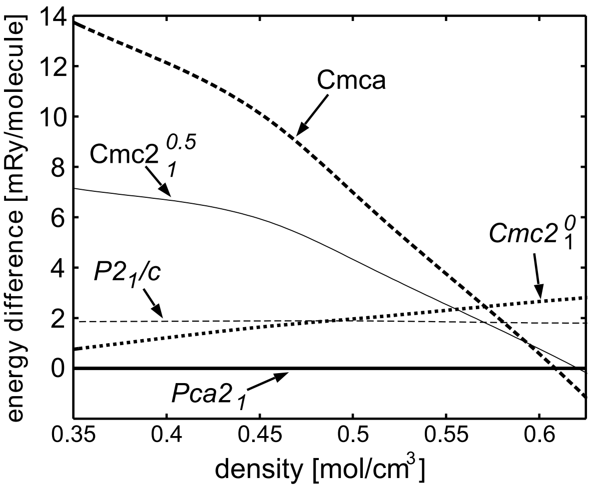

FIG. 4. EXX total energies of possible structures of molecular hydrogen, relative to the energy of the $Pca2_1$ structure.

gaps by a dynamic level-repulsion effect. Third, relative energies of different structures are changed. QMC calculations [6] and work by Straus and Ashcroft [13] suggest that zero-point motion favors isotropic structures (in our case, $Pca2_1$, $P2_1/c$, and $Cmc2_1^0$) with respect to anisotropic ones like $Cmca$. Including all these effects, we expect the metallization pressure to increase to $\gtrsim$400 GPa.

Another possibility is the metallization by a structural transition to a possible monatomic phase. A comparison of enthalpies derived from various experimental equations of state with QMC calculations [6] for hydrogen in the diamond phase yields dissociation pressures between 300 and 620 GPa [5,6]. The large range is due to the extreme sensitivity of the transition point to the form of the equation of state. Thus we can conclude only that our calculated metallization pressure is in the same range as possible transitions to other structures. However, this does not affect our main point that up to pressures of at least 400 GPa, molecular hydrogen is predicted to be stable and insulating.

In summary, we have investigated band gaps and total energies of possible candidate structures for compressed molecular hydrogen using a Kohn-Sham density-functional scheme (EXX) that treats exchange interactions exactly. EXX leads to band gaps that are 1–2 eV higher than in LDA (similar to gaps found recently using an approximate GW approach [15]) and, in addition, predicts changes of the relative energies of structures near the metal-insulator transition. In contrast to LDA and GGA calculations, the energetically preferred structure has $Pca2_1$ symmetry up to density 0.61 mol/cm^3 (pressure $\approx$ 400–450 GPa). In this structure there is the possibility of metallization via band overlap, which is here found to occur at $\approx$400 GPa. Above this pressure there are three possibilities: a metallic molecular phase as described here; some new molecular phase that is more stable and insulating; or a transition to an atomic phase expected to be metallic.

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