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Parameter-free calculation of single-particle electronic excitations in YH_3

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In recent optical experiments for YH_3 , a large band gap of almost 3 eV has been observed. In contrast, calculations within the local density approximation (LDA) result in a semimetallic band structure with a band overlap near the Fermi level of more than 1 eV. This unusually large discrepancy between the LDA results and experiment has led to suggestions that strong local correlation effects, similar to those found in transition metal oxides, are important in YH_3 . Here we conclude from parameter-free quasi-particle calculations within the *GW* approximation that YH_3 is essentially a conventional semiconductor. We argue that the experimental results can be fully understood in band structure terms without invoking strong local correlations. The unusually large error in the band structure made by LDA is traced to its poor description of the electronic structure of the hydrogen atom. Our *GW* results predict a fundamental band gap of only 1 eV and an optical gap of 2.6 eV, the difference being due to vanishing matrix elements for optical transitions at lower energies. Our prediction of a small fundamental gap could be experimentally confirmed by a combination of photoemission and inverse photoemission experiments.

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I. INTRODUCTION

Of the reversible effects recently found on exposing various metals to hydrogen,^{1,2} the most striking must surely be the “switchable mirror” effect discovered by Huiberts *et al.*³ The “mirror” essentially consists of a thin layer of yttrium (or lanthanum, or any rare earth metal) on top of a transparent (glass) substrate, which can be loaded with hydrogen by exposing it to hydrogen gas³ or by electrochemical techniques.⁴ The switching effect was first discovered in yttrium, which is probably still the material studied in most detail experimentally. On exposure to hydrogen, yttrium dihydride is easily formed. Similar to yttrium, YH_2 is a metal and it reflects light in the visible spectrum. If the amount of hydrogen in the yttrium film is increased, YH_x exhibits a metal-insulator (MI) transition at a hydrogen-to-yttrium ratio x of about 2.8. The material becomes transparent to visible light and its resistivity increases by at least two orders of magnitude.⁵ The MI transition is reversible in the sense that the metallic dihydride phase can be readily recovered (for instance, by reducing the hydrogen pressure), hence the name “switchable mirror.” It has attracted a lot of interest as a very spectacular example of a metal-insulator transition and for its technological application potential.

Before the effect can be used in practical applications, a number of properties must be improved. Since the initial discovery of the effect, switching times have been reduced by using multilayer configurations.⁶ The color neutrality as well as the contrast ratios between transparent and reflecting phases have been improved by using alloys which contain magnesium.⁷ This considerable progress has been achieved largely empirically. A better understanding of the principles

underlying the MI transition in the switchable mirror films should help efforts to improve their switching properties.

Yttrium dihydride in its bulk crystalline form has been studied in detail. Its optical and electrical properties were measured by Weaver *et al.*^{8,9} and have been successfully interpreted on the basis of first-principles band structure calculations by Peterman *et al.*¹⁰ Much less is known about the trihydride phase since bulk samples disintegrate on absorbing the additional, third hydrogen. Indeed, it was the mechanical stability of thin film samples that was the key to Huiberts’ discovery.³ Moreover it is very difficult to obtain truly stoichiometric YH_3 because this requires enormous hydrogen pressures. So far, samples could only be loaded up to $\text{YH}_{3-\delta}$ with $\delta \approx 0.01$.¹¹ From the position of the absorption edge and its dependence on δ it was concluded that YH_3 has a large optical gap of about 2.8 eV.^{12,13} Revised values were recently reported: 2.66 eV by Lee and Shin¹⁴ and 2.63 ± 0.03 eV by van Gogh *et al.*¹⁵ However, the size of the fundamental band gap is not known to date. There is a large increase in the resistivity upon formation of the trihydride phase which is inversely proportional to δ .¹¹ From this and from the increase of the resistivity with decreasing temperature (negative temperature coefficient), it could be concluded that YH_3 was a semiconductor. However, whereas for ordinary semiconductors the size of the fundamental band gap can be extracted from temperature-dependent resistivity measurements, such experiments are difficult to interpret for yttrium-hydride because hydrogen tends to be lost from the thin films when the temperature is increased.⁵ The measurements by Huiberts *et al.*¹¹ actually show an unexpected logarithmic temperature dependence. Such a temperature dependence is characteristic of weak localization in two dimensions, albeit at much lower temperatures. In the

present case it has been attributed to the temperature induced formation of hydrogen vacancies which order in defect-rich planes and form a modulated structure. In this scenario, the weak localization occurs in the conducting hydrogen-deficient phase sandwiched between insulating trihydride planes.

In YH_x the MI transition is accompanied by a structural phase change; YH_2 is cubic and YH_3 is hexagonal (as is pure yttrium metal). Since its discovery in YH_x , the MI transition has been observed in other metal-hydride materials, where it is *not* accompanied by a structural phase change. For example, LaH_x also exhibits a MI transition when x is increased from 2 to 3, but the material is cubic in both dihydride and trihydride phases. This suggests that the structural phase change from cubic to hexagonal in YH_x is not essential for the MI transition to occur, and that the origin of the latter is likely to be of an electronic nature.

A simplified picture of the electronic structure of YH_x is constructed as follows. The atomic configuration of yttrium is $[\text{Kr}]5s^24d^1$. In solid metallic yttrium the three valence electrons occupy bands which are derived from the atomic $5s$ and $4d$ states and these valence bands are only partially occupied. Hydrogen introduces additional bands and since it is more electronegative than yttrium one might expect these hydrogen bands to be lower in energy than the yttrium valence bands. Each hydrogen atom brings with it only one electron, so each hydrogen band can accommodate an extra electron. In YH_2 two of the three yttrium valence electrons are transferred to the lower lying “hydrogen” bands. The third yttrium electron stays in an “yttrium” band and YH_2 is a metal. In YH_3 the third yttrium electron is also transferred to the hydrogen bands and there is an energy gap if the hydrogen bands are separated in energy from the yttrium valence bands. This basically ionic model is appealing but too naive. Considering the chemistry of hydrogen more generally, the ionic species H^- is rarely observed and one would expect the bond to a hydrogen atom to involve a considerable covalent component. In the solid state this would result in hybridization between the hydrogen and yttrium bands, which spoils the simple ionic model discussed above.

Indeed this simple model of the electronic structure of YH_3 was not found in recent state-of-the-art band structures calculated with the local density approximation (LDA) or density functional theory (DFT). DFT-LDA calculations for YH_3 in the so-called HoD_3 structure, which is the lattice structure deduced from experiment,^{16–18} predict a (large) overlap of the yttrium and hydrogen bands at the Fermi level.^{19,20} Similarly, the best LDA calculations available for LaH_3 at the time predicted a tiny indirect band gap of 3 meV and a direct gap of 0.17 eV (Ref. 21) or a small band overlap.²⁰ These calculations clearly contradict the experimental results. The failure of LDA calculations to predict gaps for the trihydrides motivated theorists to propose alternative explanations for the band gaps found in YH_3 and LaH_3 whereby two basically different mechanisms were put forward. The “weak correlation” proposal suggested that the solution should be sought in an improved treatment of the electronic excitations based on standard electron gas theory combined with electron-phonon coupling. The “strong cor-

relation” proposal suggested that the description of the electron-electron interaction on an atomic length scale was the key to understanding the insulating state of the trihydrides.

In their “weak correlation” proposal,²² Kelly *et al.* argued that the zero-value band gap found for LaH_3 made it very similar to Ge which also has a vanishing gap in LDA. The reason for this discrepancy is well understood: it results from an unjustified interpretation of the Kohn-Sham eigenvalues of DFT as excitation energies. LDA band structures are known to systematically underestimate the band gaps of semiconductors and insulators—the so-called “band gap” problem,^{23,24} and can even predict a material to be a metal rather than a semiconductor as in the case of germanium. To calculate single-particle excitation energies, a quasiparticle equation should be solved in which the local, energy-independent exchange-correlation potential of DFT is replaced by a nonlocal, energy-dependent self-energy. Approximations based on electron-gas theory—such as the *GW* approximation to be discussed below—reproduce the experimental band gaps of semiconductors and insulators very well. By analogy with conventional semiconductors, Kelly *et al.* argued that such a correction should result in a band gap for LaH_3 but would by itself be insufficient to resolve the much larger discrepancy found for YH_3 . Therefore, in addition to the quasiparticle correction, they suggested that electron-phonon coupling played a role in YH_3 . LDA total energy calculations in which the lattice structure is optimized predict that a symmetry lowering of the HoD_3 structure leads to a slightly lower total energy (without increasing the size of the unit cell). This Jahn-Teller-like distortion leads to a band gap which would qualitatively agree with the experimental data.²² However, the calculated symmetry-breaking hydrogen displacements have not been confirmed by diffraction experiments, neither for bulk powder samples²⁵ nor for thin films^{26,27} although establishing the positions of all atoms uniquely from the diffraction data has proved to be a difficult task which has still not been resolved satisfactorily.^{28–30} To further complicate matters, we have in the meantime shown that neutron vibrational spectroscopy data can be more easily interpreted in terms of a broken symmetry structure than in terms of the HoD_3 structure.³¹ Very recent Raman effect studies of optical phonons in YH_3 and YD_3 provided the first clearcut experimental support for symmetry breaking.³²

The second explanation for the large gap in YH_3 and LaH_3 involves strong local electron-electron interactions. The discrepancy between the calculated band overlap and the observed optical gap of YH_3 is almost 4 eV. This is comparable to what is found in transition metal oxides such as NiO . In the latter material strong on-site correlations between localized d electrons play an important role and are poorly described by the LDA. Based on this analogy, it was suggested that YH_3 is a strongly correlated system with strong on-site interactions between two electrons on a hydrogen site. A number of groups have pursued this idea and have studied model Hamiltonians of a nearest neighbor tight-binding type, modified by on-site and/or nearest neighbor two-electron terms. The parameters in these models are then fitted to results obtained from (constrained) LDA calcula-

tions, and/or from molecular calculations that incorporate correlation explicitly, or have been simply estimated. Most of the focus has been on LaH_3 because its cubic structure makes it much easier to treat.

Wang and Chen considered a lattice of hydrogen atoms including on-site (Hubbard) and nearest-neighbor two-electron Coulomb interactions, which suppress the accumulation of electrons on hydrogen sites.³³ Exact diagonalization of this Hamiltonian for a cluster of hydrogen atoms does not produce a gap, so they concluded that LaH_3 cannot be viewed as a Hubbard-type correlation-driven insulator.

Ng *et al.*³⁴ adopted a quite different point of view and proposed a model which starts from doubly occupied hydrogen sites, i.e., H^- ions. As well as the hydrogen s states, they include the La $5d$ states and the nearest neighbor hybridization of these metal atom states with hydrogen. Correlation is essentially introduced by excluding doubly unoccupied hydrogen sites (H^+ configurations). Within a Gutzwiller approach they show that this leads to a substantial narrowing of the valence bands. Furthermore, they lower the on-site energies of the hydrogen sites by 0.7 eV, which is the electron affinity of a free hydrogen atom, since it is well known that LDA calculations do not give a positive electron affinity. The combination of this on-site shift and the reduced band widths produces a large band gap of 2.1 eV.³⁴

The model of Eder *et al.*³⁵ for YH_3 is also essentially a hydrogen-lattice model. In addition to an on-site Hubbard term it includes a two-electron term which describes the hopping between a hydrogen and a nearest neighbor yttrium site and depends upon the occupation number of the hydrogen site. Exact diagonalization of this Hamiltonian for a one-dimensional cyclic cluster yields a band structure that can be fitted rather well by a mean-field approximation to the same Hamiltonian. The mean-field averaged hopping between adjacent hydrogen and yttrium sites lowers the effective on-site potential on the hydrogen sites. This has the effect of shifting the valence bands down and opening up a band gap of about 2 eV for YH_3 in the simplified LaF_3 structure used in this study. In general one expects such a shift of the on-site potential to be very model and parameter dependent. For instance *all* the two-electron terms discussed by Eder *et al.* are included in a mean-field way in a self-consistent (parameter-free) LDA calculation yet the latter fails to produce a gap.

In all of these model approaches a crucial role is assigned to rather different forms of electron correlation. Because only a very limited number of the two-electron terms can be included in any calculation, the final results of the calculations rely heavily on the choice of parameters in the model. Since the main goal of these calculations is to improve upon the LDA calculations, it is surprising that not more attention is paid to the more obvious shortcomings of an LDA calculation. In the first place there is a well-known problem with the LDA lowest Kohn-Sham level in the single electron hydrogen atom.³⁶ Although the total energy of H^0 is near the expected value of -1 Ry, the one-electron energy level lies at ~ -0.5 Ry instead of at -1 Ry. In an LDA calculation one therefore expects the bands derived from the atomic hydrogen $1s$ state to be positioned too high in energy. Correcting for this artifact might by itself produce a gap in YH_3 . The

size of the correction would depend of course on the effective valence of hydrogen in YH_3 and the shift of 0.7 eV proposed by Ng *et al.*³⁴ seems to be only a lower bound. In the second place there is the “band gap” problem of LDA calculations discussed above. Finally, we note that the quoted experimental gap is deduced from optical experiments so that, depending on the optical matrix elements the optical gap may be very different from the fundamental band gap deduced from a band structure. As an example, the fundamental gap in silicon is 1.2 eV, whereas the direct optical gap is 3.4 eV.

Quasiparticle calculations within the so-called GW approximation are a practical means to obtain accurate band structures without using arbitrary fit parameters,^{37,38} and accurate band gaps have been obtained for a wide range of semiconductors and insulators using this scheme.^{37,38} Remarkably, GW calculations even produce not unreasonable gaps for materials with strong on-site interactions such as NiO (Ref. 39) and MnO .⁴⁰ In this paper we apply the GW method to the band gap problem in YH_3 giving a fuller account of calculations recently presented.⁴¹ In Sec. II the GW method and the computational techniques are explained. Section III contains the results of the GW calculations for the various possible structures of YH_3 . Finally, in Sec. IV we compare our work to the results of another recent theoretical study also based on the GW approximation.⁴²

II. THEORY

A. GW calculations

Recent reviews of the GW method can be found in Refs. 37 and 38; here we give only as much detail as is needed to reproduce the calculations and make the paper self-contained. Single-particle excitation energies can be obtained from the one-particle Green's function which describes the propagation of an extra particle (electron or hole) added to a system of particles in its ground state. Since calculating wave functions for a many-particle system is a formidable, and in general an impossible task, the Green's function is usually approximated via a many-body perturbation expansion. The electron-electron Coulomb interaction V is treated as a perturbation to a reference system of (effectively) noninteracting electrons. The latter defines a noninteracting Green's function G_0 , which is easily calculated, and the Green's function G of the interacting system can be found by solving Dyson's equation

$$G(\mathbf{r}_1, \mathbf{r}_2, \omega) = G_0(\mathbf{r}_1, \mathbf{r}_2, \omega) + \int d\mathbf{r}_3 d\mathbf{r}_4 G_0(\mathbf{r}_1, \mathbf{r}_3, \omega) \times \Sigma(\mathbf{r}_3, \mathbf{r}_4, \omega) G(\mathbf{r}_4, \mathbf{r}_2, \omega), \quad (1)$$

where $\mathbf{r}_1, \mathbf{r}_2$ are space variables and ω is a frequency (or energy) variable (Hartree atomic units are used throughout this paper). The self-energy Σ is known only in terms of a perturbation series in G_0 and the electron-electron Coulomb interaction V . The latter interaction is strong and the perturbation series contains terms that individually are divergent. This difficulty can only be avoided by applying a scheme in which such terms are carefully (re)summed to obtain a con-

vergent (partial) result. One such scheme was given by Hedin³⁷ as a set of equations in which the self-energy Σ is expressed as an expansion in the Green's function G and the *dynamically screened* electron-electron interaction W . The first term in the expansion for Σ is the screened exchange interaction, and is symbolically denoted by GW . In practical calculations the expansion is usually cut off after this first term. As the reference system of noninteracting electrons one normally uses the results of a DFT-LDA calculation, since important parts of the electron-electron interaction, such as the Hartree potential, are then already included. In most GW calculations reported in the literature, both G and W are also constructed at the LDA level, where the random phase approximation (RPA) is used for setting up W . Quite often most of the spectral density ($\sim \text{Im } G$) of the interacting electron system can be represented by a set of relatively sharp peaks, each of which has a one-to-one correspondence to a peak in the spectral density of the noninteracting reference system. If this is the case, then each such peak can be identified with a particle-like excitation and is called a quasiparticle peak. In the quasiparticle approximation (QPA) one assumes that the spectral density can be approximated by the quasiparticle peaks only.

Initially only applied to model systems such as the homogeneous electron gas, the GW method was first applied to real materials in the mid 1980's, to silicon by Hybertsen and Louie,⁴³ and by Godby, Schlüter, and Sham,⁴⁴ to germanium by von der Linden and Horsch.⁴⁵ In all of these cases GW predicted band gaps in close agreement with the experimental values. At that stage GW calculations were computationally very demanding and only applicable to relatively simple materials with small unit cells and high symmetries, such as silicon and germanium. In the meantime, computational resources have increased enormously and considerable progress has been made in developing more efficient computational algorithms, which has enabled parameter-free GW calculations to become feasible for more complex systems with large unit cells.

B. Implementation

An efficient implementation of the GW scheme was introduced by Rojas *et al.*,⁴⁶ and described recently in detail by Rieger *et al.*⁴⁷ In this so-called real-space imaginary-time method each computational step is performed either in real or reciprocal space, depending on which representation allows that particular step to be carried out most efficiently and fast Fourier transforms (FFT's) are used to switch between real and reciprocal space representations. The method uses the fact that the relevant quantities are smooth functions of imaginary time or frequency, whereas they are nonanalytic along the real axis and thus tedious to represent numerically. Most numerical operations are thus performed along the imaginary axis and only in the final stage is the result analytically continued to the real axis.

We have developed a GW code for three-dimensional (3D) crystals, which efficiently exploits lattice periodicity and the full space group symmetry of a particular solid. It is essentially based upon the real-space imaginary-time

method, along with the mixed-space representation for non-local operators.⁴⁸ In the QPA the Green's function is approximated by

$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_{n\mathbf{k}} Z_{n\mathbf{k}} \frac{\Psi_{n\mathbf{k}}(\mathbf{r}) \Psi_{n\mathbf{k}}^*(\mathbf{r}')}{\omega - E_{n\mathbf{k}}}. \quad (2)$$

Using this expression, the quasiparticle wave functions $\Psi_{n\mathbf{k}}(\mathbf{r})$ and energies $E_{n\mathbf{k}}$ can be obtained from Dyson's equation, Eq. (1), which simplifies to the so-called quasiparticle equation (QPE)

$$\left(-\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) \right) \Psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', E_{n\mathbf{k}}) \Psi_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}} \Psi_{n\mathbf{k}}(\mathbf{r}), \quad (3)$$

where $V_{\text{ext}}(\mathbf{r})$ is the "external" potential due to the nuclei, and $V_H(\mathbf{r})$ is the Hartree potential; $Z_{n\mathbf{k}}$ are the quasiparticle (QP) weights given by the expression $Z_{n\mathbf{k}} = [1 - dI(\omega)/d\omega|_{\omega=E_{n\mathbf{k}}}]^{-1}$ with $I(\omega) = \iint d\mathbf{r} d\mathbf{r}' \Psi_{n\mathbf{k}}^*(\mathbf{r}) \times \Sigma(\mathbf{r}, \mathbf{r}', \omega) \Psi_{n\mathbf{k}}(\mathbf{r}')$. Since the self-energy Σ is non-Hermitian, the "eigenvalues" $E_{n\mathbf{k}}$ are in general complex. Their real parts give the positions of the QP peaks in the spectral density ($\sim \text{Im } G$) which constitute the usual band structure (the imaginary parts give the peak widths or QP lifetimes). The self-energy Σ is approximated by the screened exchange interaction, which becomes a simple multiplication of G (or G_0) and W in the real-space imaginary-time domain [see Eq. (9) below].

As the reference system of non-interacting electrons we use the results of a DFT-LDA calculation. The LDA wave functions $\phi_{n\mathbf{k}}$ and Kohn-Sham eigenvalues $\epsilon_{n\mathbf{k}}$ are used to set up the Green's function G_0 and the screened interaction W from which the self-energy Σ is calculated. In order to solve the QPE, Eq. (3), it is transformed into a matrix "eigenvalue" equation using the LDA wave functions as a basis set in which the QP wave functions are expanded. The resulting matrix is usually almost diagonal, which simplifies solving the QPE considerably. However, Σ still depends explicitly upon the QP energies so the QPE has to be solved iteratively.

In more detail, the LDA Green's function in the imaginary time domain is given by

$$G_0(\mathbf{r}, \mathbf{r}', i\tau) = \begin{cases} i \sum_{n\mathbf{k}}^{\text{occ}} \phi_{n\mathbf{k}}(\mathbf{r}) \phi_{n\mathbf{k}}^*(\mathbf{r}') e^{(\epsilon_{n\mathbf{k}} - \epsilon_F)\tau}, & \tau > 0, \\ -i \sum_{n\mathbf{k}}^{\text{unocc}} \phi_{n\mathbf{k}}(\mathbf{r}) \phi_{n\mathbf{k}}^*(\mathbf{r}') e^{(\epsilon_{n\mathbf{k}} - \epsilon_F)\tau}, & \tau < 0, \end{cases} \quad (4)$$

where ϵ_F is the Fermi level. In setting up this Green's function, we need to truncate the summation over the unoccupied bands. This is valid since the exponent becomes very small for unoccupied states with high energies. N_{band} is the total number of (occupied and unoccupied) bands included and it is one of the parameters that determines the numerical con-

vergence. Later on we will be using numerical fast Fourier transforms (FFT's) to transform from real to reciprocal space so both $\mathbf{r}$ and $\mathbf{r}'$ are chosen on a regular real-space grid that is commensurate with the unit cell of the system. The time τ is sampled on an exponential grid whose spacing increases with increasing time. The use of an exponential grid is efficient because it has a high density of sampling points where there is most structure and a lower density where the functions are smoother.

The dynamically screened interaction is obtained in terms of the polarization propagator P in the RPA approximation, constructed in real space and imaginary time

$$P(\mathbf{r}, \mathbf{r}', i\tau) = -2iG(\mathbf{r}, \mathbf{r}', i\tau)G(\mathbf{r}', \mathbf{r}, -i\tau). \quad (5)$$

In a non-self-consistent calculation (or in the first step of a self-consistent calculation, see the following section), G is replaced by G_0 in this expression. The nonlocal quantity P has translational symmetry if the same lattice vector $\mathbf{R}$ is added to both $\mathbf{r}$ and $\mathbf{r}'$. In the mixed-space representation, we use a fully periodic quantity $P_{\mathbf{k}}(\mathbf{r}, \mathbf{r}', i\tau)$, defined by

$$P_{\mathbf{k}}(\mathbf{r}, \mathbf{r}', i\tau) = \sum_{\mathbf{R} \in \text{IC}} P(\mathbf{r} + \mathbf{R}, \mathbf{r}', i\tau) e^{-i\mathbf{k} \cdot (\mathbf{r} + \mathbf{R} - \mathbf{r}')} \quad (6)$$

which has the property $P_{\mathbf{k}}(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}', i\tau) = P_{\mathbf{k}}(\mathbf{r}, \mathbf{r}', i\tau)$. In principle, the sum over $\mathbf{R}$ runs over all lattice vectors; in practice we can assume that $P(\mathbf{r}, \mathbf{r}', i\tau)$ vanishes beyond a maximum distance $|\mathbf{r} - \mathbf{r}'|$. This distance defines a supercell called the interaction cell (IC). The sum over $\mathbf{R}$ can thus be restricted to the $N_{\mathbf{R}}$ lattice vectors within the interaction cell. The interaction cell defines a corresponding $\mathbf{k}$ grid in the first Brillouin zone (which is of course determined by the true unit cell of the system). $P_{\mathbf{k}}(\mathbf{r}, \mathbf{r}', i\tau)$ only needs to be evaluated for these $\mathbf{k}$ -grid points and for both $\mathbf{r}$ and $\mathbf{r}'$ within the unit cell. The inverse transformation is given by

$$P(\mathbf{r}, \mathbf{r}', i\tau) = \frac{1}{N_{\mathbf{R}}} \sum_{\mathbf{k} \in \text{BZ}} P_{\mathbf{k}}(\mathbf{r}, \mathbf{r}', i\tau) e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')}. \quad (7)$$

In the next step the polarization propagator in the mixed-space representation is Fourier transformed numerically to reciprocal space and to imaginary frequencies $P_{\mathbf{k}}(\mathbf{r}, \mathbf{r}', i\tau) \rightarrow P_{\mathbf{k}}(\mathbf{G}, \mathbf{G}', i\omega)$. In order to perform the Fourier transform the exponential time grid is interpolated onto a linear grid with double the number of grid points; the latter grid is characterized by the number of points N_t and their spacing Δt . The Coulomb interaction is Fourier transformed in a similar way, $|\mathbf{r} - \mathbf{r}'|^{-1} \rightarrow V_{\mathbf{k}}(\mathbf{G}, \mathbf{G}')$, and the screened interaction W is constructed from

$$W_{\mathbf{k}}(\mathbf{G}, \mathbf{G}', i\omega) = [V_{\mathbf{k}}^{-1}(\mathbf{G}, \mathbf{G}') - P_{\mathbf{k}}(\mathbf{G}, \mathbf{G}', i\omega)]^{-1}. \quad (8)$$

Additional technical details concerning the treatment of the Coulomb and the screened interaction can be found in Ref. 49. The screened interaction is then transformed back to the real-space and imaginary time domains and multiplied by G in order to obtain the self-energy operator Σ in the GW -approximation, according to

$$\Sigma(\mathbf{r}, \mathbf{r}', i\tau) = iG(\mathbf{r}, \mathbf{r}', i\tau)W(\mathbf{r}, \mathbf{r}', i\tau), \quad (9)$$

where again in a non-self-consistent calculation G is replaced by G_0 . Subsequently, the matrix elements of Σ on the basis of the LDA wave functions are calculated, $\Sigma_{kn'n'}(i\tau) = \iint d\mathbf{r} d\mathbf{r}' \phi_{n\mathbf{k}}^*(\mathbf{r}) \Sigma(\mathbf{r}, \mathbf{r}', i\tau) \phi_{n'\mathbf{k}'}(\mathbf{r}')$. Each of these matrix elements is Fourier transformed to the imaginary frequency domain, fitted to an analytical function and continued to the real axis. Simple two-pole expressions are used for these fits. The QPE, Eq. (3), in its matrix representation is then solved iteratively to obtain the QP energies and wave functions.

The accuracy of the numerical procedure is determined by (a) N_{band} , the total number of bands used to calculate the Green's function, Eq. (4), (b) N_t , Δt , the number of grid points in the time domain and their spacing, (c) the spacing of the grid points $\mathbf{r}$ in real space, (d) the size of the interaction cell, and (e) the accuracy of the analytical fit to the matrix elements of Σ .

C. Self-consistency

Hedin formulated his equations as a self-consistent scheme.³⁷ This means that in principle GW calculations can be iterated until the G which is obtained as the solution of Dyson's equation, Eq. (1), is identical to the G which is used in the construction of Σ , Eq. (9). The common experience, however, is that the results of a fully self-consistent GW calculation are poorer than those of a "single shot" procedure in which Σ is constructed from G_0 and W at the LDA level. This has been demonstrated in detail for the electron gas,⁵⁰ for a model one-dimensional semiconductor⁵¹ and recently also for silicon.⁵² Use of the complete, self-consistent G [without invoking the QPA of Eq. 2] leads to a disappearance of the plasmon satellite peak, which is unphysical, and yields band gaps that are severely overestimated. It is believed that incorporating higher order diagrams in the many-body perturbation series by vertex corrections will overcome these shortcomings, but at present this is computationally too demanding for calculations on real materials. From a formal point of view a "single shot" GW calculation is not entirely satisfactory, since the LDA calculation represents a fairly arbitrary reference system. Although the QP wave functions $\Psi_{n\mathbf{k}}(\mathbf{r})$ are very often practically identical to the LDA wave functions $\phi_{n\mathbf{k}}(\mathbf{r})$, the QP energies $E_{n\mathbf{k}}$ are certainly different from the Kohn-Sham eigenvalues $\epsilon_{n\mathbf{k}}$, which means that the QP Green's function, Eq. (2), certainly differs from its LDA counterpart. More disturbing from a practical point of view is that the LDA calculation can wrongly produce a metallic state for a material which is an insulator.⁴² The LDA results then severely overestimate the screening and produce a screened interaction W that is too weak. This ultimately results in a band gap from a "single shot" GW calculation that is severely underestimated.^{39,42}

The commonly adopted procedure is called "best G , best W " and is based upon a partial inclusion of self-consistency effects. The QPA is used for G , Eq. (2). To calculate Σ via Eqs. (5)–(9), G is further approximated by setting the QP weights to unity, $Z_{n\mathbf{k}} = 1$, in order to obey the sum rule for the spectral density, and by using only the real part of the (generally complex) QP energies $E_{n\mathbf{k}}$. This "best G " now has the same form as the G extracted from an LDA calculation.

tion. It can easily be updated by replacing the LDA $\phi_{n\mathbf{k}}(\mathbf{r})$ and $\epsilon_{n\mathbf{k}}$ in Eq. (4) by the solutions $\Psi_{n\mathbf{k}}(\mathbf{r})$ and $\text{Re}E_{n\mathbf{k}}$ of the QPE, Eq. (2). Once the updated Σ has been constructed using Eqs. (5)–(9), the QPE, Eq. (2), can be solved again. This whole process can be iterated until self-consistency is reached. The “best G ” now describes a reference system of non-interacting electrons that is “closest” to the interacting electron system. This procedure presents a solution for describing a system where LDA does not give a good reference system for the reasons explained above.

Sometimes it is sufficient to update the energies $\text{Re}E_{n\mathbf{k}}$ only, as in the pioneering work of Hybertsen and Louie.⁴³ If the QP wave functions differ considerably from the LDA wave functions they must be updated as well. Aryasetiawan and Gunnarsson have found NiO to be a material where this is required and have treated the required self-consistency using some extra approximations.³⁹ The reference system is modified by introducing an additional potential in the LDA calculation which anticipates the changes in the wave functions and energy spectrum resulting from the GW calculation. They iterate their combined scheme of LDA and GW calculations until the band gap is identical in both calculations. This criterion for convergence is somewhat arbitrary since states with energies which do not define the gap may still change considerably in subsequent iterations. Very recently Miyake *et al.*⁴² have used the same approach for YH_3 .

Updating W via Eqs. (4)–(8) is unavoidable if LDA calculations wrongly predict a material to be metallic. Sometimes this problem has been circumvented by using a model screened interaction constructed from experimental instead of LDA data. This approach has been used for InSb and InAs, which both have a negative gap in LDA, and the results are satisfactory.⁵³ Alternatively one may use the approach of Aryasetiawan and Gunnarsson.³⁹ We opt for an approach in which the QP energies and if necessary the QP wave functions, are updated both in G and in W in each cycle until self-consistency is reached. This approach embodies the “best G , best W ” idea for the case in which LDA incorrectly gives a metallic state without losing the advantages of the QPA in practical calculations. Our scheme requires more computational effort than the approach of Aryasetiawan and Gunnarsson, because we need to recalculate the full QP spectrum (i.e., all the N_{band} occupied and unoccupied bands) in each cycle, but it avoids some of the approximations of the latter approach.

III. RESULTS

We have tested our code and self-consistent procedure on silicon because its properties have been studied extensively both experimentally and theoretically. The main results of these tests are summarized in the Appendix.

From neutron diffraction experiments it has been concluded that YH_3 has the HoD_3 structure. This is a complicated lattice structure with 24 atoms in the unit cell. It can be viewed as originating from the much simpler so-called LaF_3 structure by a distortion of the hydrogen sublattice which triples the size of the unit cell.¹⁹ We use the simple LaF_3 unit cell, which contains only eight atoms, as a convenient start-

FIG. 1. Schematic representation of YH_3 in the HoD_3 structure. (a) Shows a cut through the ab metal plane; the large circles represent the yttrium atoms, the small circles the metal-plane hydrogen atoms. (b) Shows a cut perpendicular to the ab plane, along the c axis, and along the dashed line in (a); only the metal-plane hydrogens are shown explicitly; the positions of the yttrium metal planes and the planes containing the tetrahedral hydrogen atoms are indicated by solid and dashed lines, respectively.

ing point for our GW calculations. We then modify the lattice structure step by step to the HoD_3 structure and explain how the GW results change accordingly. DFT-LDA calculations predict that another structure, which can be obtained from the HoD_3 structure by additionally breaking a symmetry in the hydrogen sublattice, is lower in energy. We shall also discuss GW calculations for YH_3 in this broken symmetry structure.²²

A. The lattice structures

The yttrium atoms in YH_3 form a hexagonal lattice and two out of every three hydrogen atoms occupy positions close to the ideal tetrahedral interstitial sites in this lattice. The remaining hydrogen atoms reside in or close to the planes formed by the yttrium atoms; these atoms are usually called the metal-plane hydrogen atoms. Figure 1 shows a simplified scheme of YH_3 in the HoD_3 structure indicating the yttrium metal planes and the relative positions of the tetrahedral and metal-plane hydrogen atoms. The main difference between the possible lattice structures is in the positions of these metal-plane hydrogens. This is shown schematically in Fig. 2. Figure 2(a) shows the simplest possible (LaF_3) structure, in which the unit cell contains Y_2H_6 with two metal-plane hydrogen atoms. Figure 2(b) shows exactly the same structure in a unit cell which is tripled in the basal ab plane. The size of the Brillouin zone corresponding to this tripled cell is three times smaller, and the bands are folded back accordingly. We will return to this point later on. The distortion of the hydrogen lattice, which transforms the

FIG. 2. Schematic lattice structures of YH_3 . The yttrium metal planes are represented by horizontal solid lines, the open circles indicate the positions of the metal-plane hydrogens, the tetrahedral hydrogens are not shown. The rectangular boxes denote the unit cells; (c) corresponds to Fig. 1(b).

LaF_3 structure into the HoD_3 structure, takes place in this tripled cell. One third of the metal-plane hydrogens move to positions slightly above the metal planes, and another third to positions below the plane. The remaining hydrogen atoms stay exactly in the metal planes. The space group of the resulting HoD_3 structure, see Figs. 1 and 2(c), is $P\bar{3}c1$ (number 165 in the International Tables). Finally, in the broken symmetry structure *all* hydrogen atoms are displaced out of the metal planes. This is indicated in Fig. 2(d). One third of the hydrogen atoms is only slightly displaced out of the metal plane and the other hydrogens are roughly twice as far away from these planes. The size of the corresponding unit cell is identical to that of the HoD_3 structure but the symmetry is lower. The space group of the broken symmetry structure is $P6_3$ (number 173 in the International Tables).

B. Computational details

Apart from using a plane wave kinetic energy cutoff of 36 Ry, the computational details of the LDA calculations for YH_3 were the same as in Ref. 22. The nuclear potentials in Eq. (3) are replaced by pseudopotentials and only the valence states are used in Eqs. (2)–(9).⁵⁴ The DFT-LDA states are obtained using a pseudopotential/plane wave Car-Parrinello type code.⁵⁵ In the GW calculations for YH_3 in the LaF_3 structure we used a real-space grid of $(8 \times 8 \times 12)$ points in the unit cell and the number of bands was taken to be $N_{\text{band}}=200$ [see the discussion following Eq. (4)]. An interaction cell of $(6 \times 6 \times 4)$ unit cells was used and the time grid parameters were set at $N_t=40$ and $\Delta t=0.3$ [see the discussion following Eq. (6)]. By varying these numerical parameters systematically, we estimated that our QP energies are converged to within 0.1 eV. The inclusion of nondiagonal elements of the self-energy operator in the basis of LDA states was not crucial for YH_3 in the LaF_3 structure; it changes the gap in the QP spectrum by less than 0.05 eV. In

FIG. 3. LDA electron bands for YH_3 in (a) the LaF_3 structure, (b) the tripled LaF_3 structure, and (c) the HoD_3 structure. The corresponding GW band structures (d)–(f) are obtained from the LDA bands by linear interpolation of the calculated QP corrections found for the $\mathbf{k}$ points included in the GW calculation. The circles refer to the bands which are folded back from K to Γ when the Y_2H_6 unit cell is tripled. The triangles mark bands which are originally at Γ .

this case the LDA wave functions are thus a good approximation to the QP wave functions.

For the GW calculations on YH_3 in the HoD_3 and in the broken symmetry structure we used a $(12 \times 12 \times 12)$ real-space grid, a $(4 \times 4 \times 4)$ interaction cell, $N_{\text{band}}=300$, and the same time grid. Again, we estimate a convergence of the QP energies to within 0.1 eV. For instance, increasing N_{band} from 200 to 250 increased the gap in the QP spectrum for YH_3 in the HoD_3 structure by 0.04 eV and a further increase to 300 gave an additional increase of the gap by ≤ 0.02 eV. For the HoD_3 structure the nondiagonal elements of Σ also proved to be unimportant. However, for the broken symmetry structure some of these nondiagonal elements were large and had to be included. In this last case, particular QP wave functions were found to differ significantly from their LDA counterparts, as will be discussed below.

C. The LaF_3 structure

For YH_3 in the simplified LaF_3 structure, we reproduced the LDA results of Wang and Chou in all essential details.¹⁹ The results are shown in Fig. 3(a). The unit cell contains six hydrogen atoms resulting in six additional valence bands.

These states overlap and interact so strongly with the yttrium s and d bands that it is no longer very meaningful to try and distinguish separate “hydrogen” and “yttrium” bands. Purely for convenience, we will call the six lowest bands in Fig. 3(a) “hydrogen” bands and the higher bands which are well separated from these “yttrium” bands. The direct gap between the two groups of bands is about 0.6 eV at Γ and 2.3 eV at K. However, there is indirect overlap between the highest hydrogen band at Γ (indicated by the filled triangle) and the lowest yttrium band at K (represented by an open circle). Because of this overlap (of about 1.3 eV) the Fermi level cuts through these bands and, in the LDA, YH_3 is (incorrectly) predicted to be a metal.

Calculating the GW band structure self-consistently as explained in the previous section gives us considerable freedom in choosing our starting reference system. We begin by shifting the yttrium conduction bands relative to the hydrogen valence bands so as to open a gap. The Fermi level is chosen at the center of the gap. In this way we start with a screened interaction corresponding to a semiconductor. This leads to a large self-energy which speeds up the iteration process in the self-consistent calculation. We then iterate the GW scheme and update the QP energies in both G and W until the band energies near the Fermi level differ by less than 0.01 eV between two consecutive iterations. The converged band structure contains a considerable gap which is independent of the size of the gap chosen to begin with, as should be the case in a self-consistent procedure.

The final GW band structure for YH_3 in the LaF_3 structure is shown in Fig. 3 (d). For $\mathbf{k}$ points which were not explicitly included in the QP calculation, we linearly interpolated the calculated GW shifts for the LDA energies in order to produce comparable figures. This is reasonable because the calculated GW shifts are rather constant throughout the Brillouin zone for each band. As a result of the calculated GW shifts, the hydrogen bands become fully occupied and the yttrium bands unoccupied. An indirect band gap of 0.6 eV exists between these two sets of bands at the Γ and K points. The direct gap at Γ is 2.9 eV which agrees very well with the experimentally obtained optical gap for YH_3 . Because the strongest optical excitations are $\mathbf{k}$ conserving, this large direct gap would dominate an optical experiment if YH_3 had the LaF_3 structure. This is then quite comparable to the situation in silicon where the fundamental gap is only 1.2 eV and the direct gap 3.4 eV.

The overall valence band width of about 10 eV in the GW calculation is slightly larger than the LDA value of about 9 eV. This increase in band width is in strong contrast to the results of the model calculation by Ng *et al.*³⁴ for LaH_3 which predicts a large decrease compared to the LDA valence band width. GW calculations often result in band widths which are somewhat smaller than the LDA values. However, there is no general rule that an improved treatment of correlation effects will lead to a reduction of the LDA band width. Other materials are known for which GW increases the LDA band width, two examples being LiCl ⁵⁶ and CdS .⁵⁷ In any case, the fact that the band width is not drastically changed in the present GW calculation suggests that YH_3 is not strongly correlated in the sense of Ref. 34. This

suggestion is also supported by the relatively large spectral weights, indicating the strong quasiparticle character of the spectral density and thus the absence of strong correlations. The QP states of the highest valence and lowest conduction bands have spectral weights $\text{Re}Z_{nk} \approx 0.81$. The Brillouin zone average of the spectral weight averaged over the ten lowest states is 0.84.

D. The HoD_3 structure; dielectric function

As a prelude to the GW calculations for YH_3 in the HoD_3 structure we first discuss the results for YH_3 in the LaF_3 structure in an artificially tripled LaF_3 unit cell [see Fig. 2(b)]. The Brillouin zone corresponding to this tripled unit cell is three times smaller than the original Brillouin zone. Consequently, bands are folded back from different $\mathbf{k}$ points to Γ . In Fig. 3(b) we focus upon the LDA bands near the Fermi level around Γ . Two of the bands which were originally at K are now folded back to Γ in the smaller Brillouin zone. These bands are labeled with an open circle, while the filled triangle marks the band(s) which originated from Γ . As a result of this folding the indirect LDA band overlap in the Brillouin zone of the LaF_3 structure becomes a “direct” band overlap at Γ in the Brillouin zone of the tripled unit cell. We see that two pairs of bands cross the Fermi level around Γ .

The results of the GW calculation are plotted in the three times smaller Brillouin zone as well, see Fig. 3(e). The small indirect gap of YH_3 in the LaF_3 structure becomes a direct gap at Γ now. However, optical transitions between pairs of states which originate from different $\mathbf{k}$ points are of course still forbidden. The matrix elements for direct optical transitions between such bands vanish because of symmetry, and the optical gap at Γ in the Brillouin zone of the tripled unit cell is given by the gap between the valence band marked with the triangle, and the second lowest conduction band; it is 2.9 eV.

As discussed in Sec. III A the HoD_3 structure results from displacing some of the metal-plane hydrogen atoms out of the metal plane (accompanied by relaxation of the tetrahedral hydrogen atoms). This lowers the symmetry and induces an interaction between one pair of the bands which overlap near the Fermi level around Γ in the LDA; compare Figs. 3(b) and 3(c). The interaction moves both bands of this pair away from the Fermi level; the lower band is pushed down in energy and out of the energy range plotted in the figure. The other pair of bands remains essentially unchanged in the HoD_3 structure and the matrix elements for direct optical transitions between them still vanish. In the LDA calculation we find an overlap of about 1.1 eV between these bands at Γ . The GW calculation for YH_3 in the HoD_3 structure results in the opening of a direct band gap of 1.0 eV [see Fig. 3(f)], but the optical gap at Γ is still 2.9 eV; in the ΓM direction it is a few tenths of an eV smaller.⁵⁸ The overall valence band width is 9.8 eV, close to the value of 10.0 eV in the LaF_3 structure. The limited energy resolution of experimental results^{59,60} does not allow a detailed comparison to be made; the most we can say is that there is no inconsistency in the band widths. Since the calculated QP wave functions are found to be practically identical to the LDA wave functions,

FIG. 4. $\epsilon_2(\omega)$ calculated using the LDA wave functions and the shifted LDA energies, where the band separation between the yttrium and hydrogen band has been increased by 2 eV. The xx and zz elements of the dielectric tensor have been broadened.

we can use the latter to calculate the matrix elements for the electric dipole transitions which are needed to obtain the contribution of interband transitions to the imaginary part of the dielectric tensor $\epsilon_2(\omega)$. An accurate calculation of these tensor elements requires a very fine $\mathbf{k}$ grid for the Brillouin zone integration. Such a dense $\mathbf{k}$ grid is computationally too expensive for a *GW* calculation. Instead, we have approximated the contributions of direct interband transitions to $\epsilon_2(\omega)$ using shifted LDA energies on a dense ($12 \times 12 \times 10$) $\mathbf{k}$ grid. The energy separation between the centers of the yttrium and hydrogen bands is increased by a constant 2 eV. This so-called “scissors operator” is a somewhat crude approximation to the actual QP spectrum but is quite good for the states close to the Fermi level. Since it is these states that almost exclusively contribute to $\epsilon_2(\omega)$ at low energies, this procedure is quite reasonable. The results are shown in Fig. 4; the solid and dashed curves correspond to the xx and zz part of the dielectric tensor, respectively. In optical experiments on polycrystalline films only a superposition of the two components of the dielectric tensor can be measured.

From Fig. 4 it can be seen that the matrix elements for optical transitions are very small in the energy range roughly between 1 and 3 eV and the optical gap of about 2.6 eV can be clearly identified. However, there is some structure in the calculated $\epsilon_2(\omega)$ at energies below the optical gap; $\epsilon_2(\omega)$ has a tail extending downwards in energy to about 1.3 eV. This feature is related to transitions between states close to Γ which belong to the highest valence band and the lowest conduction band. Exactly at Γ transitions are symmetry forbidden but at $\mathbf{k}$ points near Γ without any symmetry they become weakly allowed. These transition probabilities will become more important when the high symmetry of the HoD_3 structure is broken, either statically or dynamically, whereby the large zero point motion of the hydrogen atoms should be considered in addition to the normal thermal motion. Very recently Van Gogh *et al.* have studied the dielectric functions of YH_3 experimentally and have observed

FIG. 5. LDA band structures along $A\Gamma$ for YH_3 in (a) the HoD_3 structure and (b) the broken symmetry structure. The corresponding *GW* band structures are given in (c) for YH_3 in the HoD_3 structure where the calculated energy shifts have been interpolated in between $\mathbf{k}$ points which are not included in the *GW* calculation and (d) for YH_3 in the broken symmetry structure, where the dashed lines are guides to the eye.

weak absorption below an optical gap of 2.6 eV.¹⁵ We speculate that this weak absorption results from such static or dynamic symmetry breaking.

E. The broken symmetry structure

Finally, we discuss the results of *GW* calculations for YH_3 in the broken symmetry structure. This structure has the lowest total energy within the LDA and the LDA spectrum has a band gap.²² However, so far this lattice structure has not been directly confirmed by, e.g., diffraction experiments but there has recently been some evidence of symmetry lowering.^{31,32} In Figs. 5(a)–5(b) we compare the LDA bands along the $A\Gamma$ direction for the HoD_3 structure and for the broken symmetry structure. The latter can be obtained from the HoD_3 structure by displacing the hydrogen atoms as discussed in Sec. III A. Breaking the symmetry of the HoD_3 structure introduces additional interactions between bands. As can be observed in Figs. 5(a)–5(b) the bands near the Fermi level which cross in the HoD_3 structure, show an avoided crossing in the broken symmetry structure. This opens up a band gap in the LDA spectrum. For other bands the changes are much smaller.

We have applied our self-consistent GW procedure to the broken symmetry structure, updating the QP energies in both G and W . The resulting GW bands along $A\Gamma$ near the Fermi level are given in Fig. 5(d); for comparison we have plotted the corresponding GW bands for YH_3 in the HoD_3 structure in Fig. 5(c). In addition to an increase in the band gap of the broken symmetry structure as a result of the GW corrections, we also find important changes in the shapes of the bands near the Fermi level as compared to the LDA bands. The avoided crossing between the highest occupied and lowest unoccupied bands which is so evident in Fig. 5(b) is absent in Fig. 5(d). Because the QP corrections of these bands are very $\mathbf{k}$ dependent the interpolation scheme used to plot the GW bands for YH_3 in the HoD_3 structure cannot be used. Therefore, the dashed lines which connect the calculated QP energies in Fig. 5(d) only serve as a guide to the eye. Since the GW calculation for YH_3 in the HoD_3 structure already opens up a gap, the symmetry breaking as such is no longer needed to do this. The GW bands of the broken symmetry structure actually quite closely resemble the GW bands of the HoD_3 structure. The change in the shape of the bands near the Fermi level in the broken symmetry structure going from the LDA to the GW results is accompanied by a change in the corresponding wave functions. For example, at Γ there is a significant mixing of the wave functions of the lowest unoccupied and highest occupied LDA bands in the corresponding QP wave functions. The lowest QP conduction wave function contains more than 20% of the highest LDA valence wave function, and conversely. The final band gap in the broken symmetry structure is about 1.4 eV and the total valence band width is 10.1 eV which is comparable to the results for both the simplified LaF_3 structure and the HoD_3 structure. Breaking the symmetry will, in general, also induce a finite oscillator strength between states for which it vanished by symmetry in the HoD_3 structure. Therefore we expect that the calculated low-energy tail in $\epsilon_2(\omega)$ (see Fig. 4) will be more pronounced in the case of a broken symmetry structure. Since other states are much less affected by the symmetry breaking the higher energy part of $\epsilon_2(\omega)$ will remain largely unchanged.

IV. DISCUSSION

In view of the failure of LDA calculations to predict a band gap for YH_3 in the HoD_3 lattice structure, strong electron-electron correlation models were proposed to explain the large gap observed in this material. The present results call into question the pivotal role of such strong correlations in opening a gap in YH_3 . Ng *et al.*³⁴ introduced a model in which large on-site correlation on the hydrogen atoms results in a large decrease of the valence band width and opens up a substantial gap. We do not find such a decrease of the band width in our GW calculations. On the contrary, our calculated band width increases slightly compared to the LDA result, which suggests rather extended hydrogen-related states.

The model of Eder *et al.* focuses on a correlation term describing the interplay between the hydrogen on-site occupancy and the delocalization of the hydrogen orbital by hy-

bridization with nearest-neighbor yttrium orbitals. Already at the mean-field level this so-called “breathing” of the hydrogen orbitals results effectively in a downward shift of the on-site hydrogen levels.³⁵ However, at the mean-field level this breathing effect is already included in LDA calculations, in contrast to the assertion made by Eder *et al.* As such it *cannot* be used to improve upon the LDA results.

There is a much more prosaic reason why on-site hydrogen energies are not described very well within LDA. It can be traced to the failure of LDA to describe the $1s$ eigenvalue of the neutral hydrogen atom. This is a well-understood artifact arising from the incomplete cancellation of the electron self-interaction by the local exchange-correlation potential.³⁶ As a result, the LDA places the $1s$ eigenvalue of atomic hydrogen at -0.5 Ry rather than at -1 Ry.⁶¹ The difference between the Y and H on-site energies is then severely underestimated which results in the band centers of the valence and conduction bands being too close and in an overlap of the bands. This is corrected for in the GW calculation. In addition there is the conventional problem in LDA band structures that semiconductor band gaps are too small. For these conventional semiconductors quasiparticle calculations within the GW approximation give quite accurate results without introducing fitting parameters. Such parameter-free calculations for YH_3 in the experimentally obtained lattice structure predict a substantial fundamental band gap of 1 eV. Because the dipole matrix elements for transitions between the highest valence and lowest conduction states vanish, the optical gap is much higher in energy, namely 2.6 eV. This difference between fundamental and optical gaps is neglected in Refs. 34 and 35.

Very recently, Miyake *et al.*⁴² also studied the quasiparticle spectrum of YH_3 by a GW calculation. Their main results were obtained for YH_3 in the hypothetical cubic BiF_3 structure and only a limited set of calculations was performed for YH_3 in the simplified LaF_3 structure making a detailed comparison difficult. Their main conclusion, similar to ours, is that weak correlation as described in the perturbative GW approximation is sufficient to open a gap. Our optical gap is in agreement with experimental (optical) data. In addition, we predict a smaller fundamental gap which could be verified by a combination of photoemission and inverse photoemission experiments.

The picture of YH_3 which we derive from our parameter-free calculations is that of a simple compound semiconductor in which on-site Coulomb correlations play a minor role and can be treated within the GW formulation of many-body perturbation theory. This interpretation is supported by the relatively large spectral weights ($\text{Re}Z_{n\mathbf{k}} \gtrsim 0.8$) of the quasiparticle peaks. We can think of constructing the solid starting with neutral H^0 and Y^0 atoms. Because the ionization energy of atomic H^0 is twice as large as that of Y^0 , charge is transferred from Y to H when the atoms interact.⁶¹ As a result, H acquires a negative charge, which is in agreement with the interpretation of electromigration experiments given in Ref. 62. This charge transfer causes the levels derived from the H $1s$ states to shift upwards in energy and the Y levels to move downwards. As usual, overlap of the valence orbitals on neighboring atoms leads to a covalent interaction and the

atomic levels broaden into bands. In addition, the charge transfer to hydrogen causes the atomic orbital to delocalize and leads to increased band width. These effects are fully accounted for by a self-consistent band model.

The present results show that symmetry-breaking hydrogen displacements are not needed to open a band gap in YH_3 . Whether or not such symmetry-breaking plays a role in YH_3 is still a subject of debate.^{31,32}

Now that we have obtained a coherent picture of the host material YH_3 , future research could profitably address the role of point defects, such as hydrogen vacancies, and their effect on the transport and optical properties. We note that although on-site electron correlation is small compared to the valence or conduction band width of YH_3 , it is not necessarily small compared to the band gap and almost certainly plays an important role in determining the charge states of hydrogen vacancies. In silicon for example, the gap states of lattice vacancies are found to have atomic-like localization,^{63,64} and consideration of on-site correlation effects is essential for understanding the behavior of vacancies. Nonetheless, these effects are not considered to play any role in determining the properties of defect-free crystalline silicon.

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APPENDIX

In order to test our GW code and to study the effect of self-consistency at different levels, we performed calculations for crystalline silicon which has been studied extensively by Hybertsen and Louie,⁴³ and by Godby, Schlüter, and Sham,⁴⁴ who found excellent agreement with experiment. More recently, very good results were also obtained by Rieger *et al.*⁴⁷ and by Fleszar and Hanke.⁶⁵ We will compare our results with those obtained recently by Rieger *et al.*; other comparisons can be found in Ref. 47. We have used a Troullier-Martins pseudopotential,⁶⁶ a plane wave kinetic energy cutoff of 25 Ry and an adequate $\mathbf{k}$ -point sampling to obtain well-converged LDA results. An LDA calculation for silicon predicts a one-electron spectrum with a band gap of about 0.5 eV, whereas the experimental gap is close to 1.2 eV.

In our GW calculations we find that the QP energies near the Fermi level are converged within 0.03 eV or better with respect to these numerical parameters if we use a $(6 \times 6 \times 6)$ real-space grid, a $(4 \times 4 \times 4)$ interaction cell, $N_{\text{band}} = 145$, $N_t = 40$, and $\Delta t = 0.3$. The QP energies agree very well with those reported by Rieger *et al.*,⁴⁷ as can be seen in Table I. The small deviations which occur already at the level of the LDA calculation come from using a slightly different pseudopotential.

In principle, when solving the QP equation, one must also include nondiagonal elements of the self-energy operator in

TABLE I. LDA and GW energies and band gaps in silicon from the present method and the results by Rieger *et al.* (Ref. 47).

band	present		Rieger	
	LDA	G_0W_0	LDA	G_0W_0
Γ_{1v}	-11.94	-11.52	-11.89	-11.57
Γ'_{25v}	0.00	0.00	0.00	0.00
Γ_{15c}	2.56	3.15	2.58	3.24
Γ'_{2c}	3.17	3.76	3.28	3.94
X_{1v}	-7.80	-7.61	-7.78	-7.67
X_{4v}	-2.84	-2.79	-2.82	-2.80
X_{1c}	0.64	1.33	0.61	1.34
L'_{2v}	-9.60	-9.33	-9.57	-9.39
L_{1v}	-6.96	-6.78	-6.96	-6.86
L'_{3v}	-1.19	-1.17	-1.17	-1.17
L_{1c}	1.44	2.06	1.46	2.14
L_{3c}	3.33	4.00	3.33	4.04
band gap	0.51	1.17	0.49	1.20

the LDA basis wave functions. For silicon it is known that these elements are small, and that the eigenfunctions of the QP equation are practically identical to the LDA wave functions. We have specifically tested this by including all non-diagonal elements between the lowest 30 bands, and find that the results for the tabulated QP energies change by less than 0.01 eV. The LDA and QP wave functions overlap by more than 99.9%. In order to test our code for hexagonal systems (YH_3 has a hexagonal unit cell) we studied bulk silicon in an artificial hexagonal unit cell containing six atoms, with its c axis along the (111) (cubic) crystal direction. The QP energies agreed very well with those obtained for the cubic unit cell.

The effect of a self-consistent Green's function is first tested by iterating the GW scheme, replacing the LDA energies in G by the calculated real parts of the QP energies from

TABLE II. Calculated QP energies for silicon at special $\mathbf{k}$ points when W is kept at the LDA level (W_0) while G is updated, and the self-consistent result (indicated by GW).

band	G_0W_0	G_1W_0	G_2W_0	GW
Γ_{1v}	-11.52	-11.54	-11.56	-11.82
Γ'_{25v}	0.00	0.00	0.00	0.00
Γ_{15c}	3.15	3.24	3.25	3.47
Γ'_{2c}	3.76	3.86	3.87	4.09
X_{1v}	-7.61	-7.63	-7.65	-7.81
X_{4v}	-2.79	-2.80	-2.80	-2.85
X_{1c}	1.32	1.40	1.41	1.61
L'_{2v}	-9.33	-9.35	-9.37	-9.58
L_{1v}	-6.78	-6.80	-6.81	-6.96
L'_{3v}	-1.17	-1.18	-1.18	-1.20
L_{1c}	2.06	2.14	2.15	2.35
L_{3c}	4.00	4.08	4.09	4.32
band gap	1.17	1.25	1.26	1.46

the previous iteration. The results of the first three iterations when only G is updated are shown in Table II. W_0 means that we keep W fixed at the LDA level. The QP energies change by about -0.01 and about 0.1 eV for the occupied and unoccupied states respectively, after the first update of G . After the second update the changes are much smaller and after the third update (not shown here) the QP energies of interest change by less than 0.01 eV. We have used the latter as a convergence criterion for the self-consistent GW calculation. The band gap is increased by about 0.1 eV by this partial self-consistent procedure, in agreement with Ref. 47.

If the LDA calculation wrongly predicts a metallic state as

in YH_3 , one has to update W as well for reasons discussed in Sec. II C. The effect of updating the QP energies in W is tested for silicon. We find that now more iterations are required to achieve self-consistency; starting from the LDA spectrum the QP energies are converged in six iterations (within 0.01 eV). The final self-consistent results when updating the energies in both G and W are also given in Table II in the column headed by GW . These self-consistent QP energies shift by up to 0.2 eV as compared to the partial self-consistent results, downwards for the occupied states and upwards for the unoccupied states. The band gap increases by approximately 0.2 eV leading to poorer agreement with experiment.

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