Weighted-density-approximation description of rare-earth trihydrides

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Density-functional calculations within the weighted density approximation (WDA) are presented for YH$_3$ and LaH$_3$. We investigate some commonly used pair-distribution functions $G$. These calculations show that within a consistent density-functional framework a substantial insulating gap can be obtained while at the same time retaining structural properties in accord with experimental data. Our WDA band structures agree with those of $GW$ approximation very well. It shows that there is no strong correlation in H 1$s$ states, and the absence of self-interaction in H 1$s$ is crucial to obtain correct band structures of these rare-earth trihydrides. But the calculated band gaps are still 1.0–2.0 eV smaller than experimental findings.

I. INTRODUCTION

The rare-earth trihydrides, $MH_3$, where $M = Y, La$–$Lu$, are the subject of considerable practical and theoretical interests. The rare earths absorb hydrogen readily and in the trihydride form have among the largest hydrogen to metal ratios of the elemental hydrides.$^1$ The fully hydrogenated materials are insulating, while those with less hydrogen are metallic, and in thin film form they can be used as switchable mirrors.$^2$ It is important to demonstrate a correct description of these trihydrides in first-principles approaches in order to validate calculations for more complex metal hydrogen systems. However, standard first-principles calculations based on density-functional theory (DFT) within the local-density (LDA) and generalized gradient (GGA) approximations incorrectly predict metallic behavior for the rare-earth trihydrides. Here we explore application of the weighted density approximation (WDA). We find a WDA that works for these materials (and others), indicating that the gap problem here is not due to unusual correlations or quasiparticle corrections, but is simply a problem with the LDA and GGA exchange correlation ($xc$) functionals.

The rare-earth dihydrides, $MH_2$, are metallic. The trihydrides on the other hand are insulating with optical gaps of the order of 2 eV, with a metal insulator transition at a hydrogen content correlated with rare-earth ionic radius.$^2$ This insulating gap of the trihydrides may be understood in terms of simple picture, in which H forms a negative ion, $H^-$, fully ionizing the metal atoms, thus forming a gap between H bands and higher lying metal $sd$ conduction bands. This simple picture is supported by infrared and photoemission measurements.$^3$ It is consistent with the fact that all the rare-earth trihydrides are insulators despite differences in the details of their crystal structures. These range from the $f_{cc}$ derived structure of LaH$_3$ to the not fully solved hexagonal structure of YH$_3$.5–8

Computations within the LDA predict a metallic band structure with substantial overlap between H and metal derived bands.$^8$–$^{11}$ This severe gap problem could be due to several possible causes: (1) use of an incorrect crystal structure; (2) an extreme case of LDA error in predicting gaps; (3) unusual correlation effects; or (4) self-interaction errors in LDA. Early attempts at resolving this discrepancy focused on crystal structure. Indeed it was shown that with optimized crystal structures, DFT calculations could yield insulating band structures for YH$_3$.12,13 Unfortunately, these relaxed structures are not consistent with diffraction measurements, and such an explanation would not explain the similar insulating properties of the other $MH_3$ compounds.

DFT is a theory of ground-state properties, and the eigenvalues of the Kohn-Sham equations cannot be equated to quasiparticle excitations.$^{14}$ Nevertheless, any nonpathological accurate approximation to the exact DFT should predict an insulating Kohn-Sham band structure, because static responses and other ground-state properties depend on the presence or absence of a gap. For example, LO-TO splitting would be present in the phonon spectrum ofionic insulator like YH$_3$ but not in a metal.

Recent studies on rare-earth trihydrides have considered electron correlation effects,$^{15}$–$^{19}$ particularly electron correlations on the H sites. However, since there are no partially occupied $d$ or $f$ orbitals in LaH$_3$ and YH$_3$, nor is there evidence that these materials are near a quantum critical point, these hydrides represent a novel class of strong correlated materials. Calculations done within the $GW$ approximation showing band gaps that are reconcilable with experiment are
obtained, both with the cubic BiF$_3$ structure (LaH$_3$) and the hexagonal HoD$_3$ structure (a simplified YH$_3$ structure). However in the $GW$ calculations, the dielectric function is inherently wrong since it comes from the LDA, where the ground state is metallic and not insulating. Also, the $GW$ calculations are very cumbersome, and it would be advantageous to a simple and fast method that gives reasonable results.

The $GW$ method approaches the problem as being most simply viewed as due to the treatment of excited states, but if the problem is due to self-interaction, it is fundamentally a ground-state problem. The LDA makes large errors in description of the one-electron hydrogen atom because of incomplete cancellation of the Hartree and xc self-interactions. One way to remove the spurious self-interactions in LDA and GGA calculations is the so-called self-interaction correction. In this approach an orbital dependent self-interaction is calculated at each step and used to create an orbital dependent single-particle Hamiltonian. This method suffers from basis set dependence, e.g., the computed correction is zero for a Bloch state representation. We explore whether one can remain within conventional ground-state DFT and obtain the proper electronic structure of rare-earth trihydrides.

II. WEIGHTED DENSITY APPROXIMATION

The weighted density approximation (WDA) (Refs. 21–23) has the exact nonlocal form of DFT expression of xc energy.

$$E_{xc}[n] = \int \int n(r)n(r') \frac{[\tilde{g}_{xc}(r,r'),n]-1}{|r-r'|} d\mathbf{r} d\mathbf{r}'. \tag{1}$$

Since the exact pair-distribution function $\tilde{g}_{xc}(r,r',n)$ is elusive, a model WDA function $G$ is made,

$$\tilde{g}_{xc}(r,r',n) - 1 = G(|r-r'|,\tilde{n}(r)), \tag{2}$$

where the weighted density $\tilde{n}(r)$ can be determined from the xc hole condition:

$$\int n(r')G(|r-r'|,\tilde{n}(r)) d\mathbf{r}' = -1. \tag{3}$$

This assures no self-interaction in a one-electron system. The WDA also gives correct results for the uniform electron gas because it reduces to the LDA in this case. However because $G_{WDA}(r,r') \neq G_{WDA}(r',r)$, the form of $V_{xc}^{WDA}$ is incorrect, and it causes wrong asymptotic behavior at large distance away from nucleus. Fortunately this error is not substantial when calculations are done at experimental structure.

In the WDA, an approximation is made for the function $G$, a natural choice of $G$ would be of a uniform system, but Mazin and Singh emphasized, based on the xc kernel, that $G$ of the uniform electron gas is not optimal. Several model forms of $G$ have been suggested, such as the Gunnarsson-Jones (G-J) (Ref. 24) ansatz, $G_{G-J}^G(r,n) = c \{1 - \exp(-|r/A|^{3k})\}$, with $k=5$; and the Gritsenko et al. (GRBA) (Ref. 26) ansatz, $G_{GRBA}^G(r,n) = c \cdot \exp(-|r/A|^{\beta})$, with $k=1.5$. In this paper, we also used a homogeneous type of $G$, and another $G-J$ type for $k=4$ ($G-J4$), which was tested by Rushton et al. for silicon.

One subtle issue in WDA implementations is shell partitioning. Although the WDA has the exact form of xc energy, it does not describe the exchange energy between core and valence states very well due to the approximate model $G$ function. Outside core regions, the core density vanishes, so does the core-valence exchange energy. However in the $GW$ scheme, because the range of integration of $G$ is similar to the size of atoms, and there is no distinction between core and valence electrons, core and valence electrons would dynamically screen valence electrons equally, and it could cause the core-valence exchange energy to be exaggerated. If the exact $G$ function for an arbitrary electron system is known, it will naturally describe intershell interactions correctly. On the other hand, the LDA can give correct intershell contributions, since the LDA depends only on local density. Based on this observation, a shell partitioning approach was proposed to guarantee the correct behavior of core-valence xc interaction, in which the valence-valence interactions are treated with the WDA, while core-core and core-valence with the LDA.

If $n_s(r)$ and $n_v(r)$ denote valence and core electron density, respectively, the xc energy

$$E_{xc}[n] = E_{xc}^{LDA}[n] + E_{xc}^{WDA}[n_v,n] - E_{xc}^{LDA}[n_s,n], \tag{4}$$

where

$$E_{xc}^{WDA}[n_v,n] = \int \int n_s(r)n_v(r') \frac{G(|r-r'|,\tilde{n}(r))}{|r-r'|} d\mathbf{r} d\mathbf{r}', \tag{5}$$

$$E_{xc}^{LDA}[n_v,n] = \int \int n_s(r)n_v(r) \frac{G(|r-r'|,n(r))}{|r-r'|} d\mathbf{r} d\mathbf{r}'. \tag{6}$$

The weighted density $\tilde{n}(r)$ can be chosen from the following sum rule

$$\int \{n_s(r')G(|r-r'|,\tilde{n}(r)) + n_v(r)G(|r-r'|,n(r))\} d\mathbf{r}' = -1. \tag{7}$$

The xc potential for core and valence states are different in that the xc energy depends on core and valence electron density explicitly. The derivation is attached in the appendix. An accurate potential makes the calculations fully consistent, so that atomic forces can be determined by the Hellmann-Feynmann theory. We found that the calculated forces within the WDA agree with numerical results of finite energy difference very well.

III. RESULTS AND DISCUSSION

A. Calculation details

The calculations were done using a plane-wave basis with pseudopotential method. Pseudopotentials were generated by Troullier and Martins scheme. We treated semicore states
TABLE I. With the calculated atomic positions and fixed $c/a$ ratio, the optimized equilibrium volumes (in Å$^3$) of hexagonal $YH_3$ ($Y_2H_6$). Here $a$, $b$, $c$, and $d$ denote uniform, GRBA, G-J, and G-J4 forms of $G$, respectively. Numbers in parentheses are the percentage deviations from experiment.

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B. Hexagonal $YH_3$

As mentioned before, although the exact structure of hexagonal $YH_3$ is still under investigation, its insulating property is believed to be an electronic property, i.e., not sensitive to the crystal structure. We studied a simplified hexagonal $LaF_3$ structure with a $Y_2H_6$ unit cell, in which $Y$ atoms form a hexagonal close-packed (hcp) structure. The measured lattice constants are $a=3.672$ Å and $c/a=1.81$. We optimized the $H$ positions using LDA and WDA (with four types of $G$), and all the results are consistent with the previous LDA result. We also optimized the equilibrium volume with fixed $c/a$ ratio. Table I shows that the WDA volumes deviate by only about 2−3% from experimental data.

The calculated bands of the LDA and WDA (with the G-J4 type of $G$) are shown in Fig. 1. The LDA predicts a direct band gap of 1.0 eV at $\Gamma$ and an overlap of 0.93 eV between $\Gamma$ and $K$, which leads to a semimetal. Our present LDA results are a little different from previous results (0.6 eV for the $\Gamma$ gap and 1.3 eV for the overlap) because we used the Hedin-Lundqvist xc function, whereas the Wigner ansatz was used previously. The WDA (with the G-J4 type of $G$) predicts a direct $\Gamma$ gap of 2.2 eV, and opens up a fundamental gap of 0.41 eV between $\Gamma$ and $K$. Thus, the WDA predicts a substantial insulating gap. Our WDA band gaps are close to the $GW$ calculations of 0.6 eV for the fundamental gap and 2.9 eV for the direct $\Gamma$ gap in the Brillouin zone of the more complicated tripled $HoD_3$ structure of $YH_3$, this indirect $\Gamma$-$K$ gap will be folded to form a direct gap at $\Gamma$ point, and they are roughly of the same order of magnitude. Thus, a small gap between $\Gamma$ and $K$ in the simple hexagonal structure makes $YH_3$ a semiconductor even in the complicated $HoD_3$ structure.

We also calculated the WDA bands with the other three $G$ functions, and the band gaps are shown in Table II. We found that the WDA with all these $G$’s gives better band gaps than the LDA. Except for the G-J4 form, the GRBA (Ref. 26) form is superior to the other two, because it predicts a larger direct $\Gamma$ gap and smaller overlap between $\Gamma$ and $K$. These results illustrate that the WDA band structure is sensitive to the choice of $G$. We compare these pair-distribution functions by drawing them together in Fig. 2, where $n = 3/(4 \pi r_s^3)$, and in the WDA calculations of $YH_3$, $0.8 < r_s < 2.3$. We found the G-J4 form has the shortest range, and the range of GRBA ansatz is shorter than the other two. Our calculations indicate that a shorter range $G$ gives larger band gaps. Interestingly, such functions, particularly GRBA, yield static responses closer to Monte Carlo results for the uniform electron gas.

C. Cubic $YH_3$ and $LaH_3$

We performed LDA and WDA (with G-J4 only) calculations on cubic $BiF_3$ structure of $YH_3$ and $LaH_3$, in which the $Y$ or $La$ atoms constitute a face-centered cubic (fcc) lattice and $H$ atoms are located at the tetrahedral and octahedral sites. Recently the insulating fcc $YH_3$ was stabilized by existence of $MgH_2$, but there are large discrepancies in the

FIG. 1. LDA and WDA (with the G-J4 type of $G$) electron bands of the hexagonal $YH_3$.

FIG. 2. Four types of the pair-distribution function $G(r,n)$ with $r_s = 0.8$ and $r_s = 2.3$.  

TABLE II. Calculated LDA and WDA (a, b, c, and d as seen in Table I) fundamental and $\Gamma$ gaps (in eV), compared with $GW$ results. A negative band gap means band overlap.
measured volumes of fcc \( \text{YH}_3 \). Ahuja et al.\(^{13}\) expected 32.2 Å\(^3\), while van der Molen et al.\(^{33}\) extrapolated 36.9 Å\(^3\) and Gogh et al.\(^{32}\) obtained 38.0 Å\(^3\). Our LDA and WDA equilibrium volumes are 32.4 Å\(^3\) and 35.2 Å\(^3\), respectively. We calculated band structure at experimental volume of 36.9 Å\(^3\). For LaH\(_3\) the measured volume 44.2 Å\(^3\) is close to both LDA and WDA results, and we used this volume to calculate band structure.

In Fig. 3 are the calculated band structures of cubic \( \text{YH}_3 \) and \( \text{LaH}_3 \). The LDA predicts that both of them are metals with direct overlaps of 1.0 eV for \( \text{YH}_3 \) and 0.46 eV for \( \text{LaH}_3 \) at \( \Gamma \) point, which agree with previous calculations.\(^{19,34}\) Contrary to the LDA, the WDA predicts that both trihydrides are semiconductors with direct \( \Gamma \) gaps of 0.19 eV and 0.80 eV for \( \text{YH}_3 \) and \( \text{LaH}_3 \), respectively. However the fundamental gaps are about 0.1 eV smaller, because the energy of lowest conduction band at \( L \) is slightly lower than that at \( \Gamma \). Our WDA band gaps are in good agreement with previous \( GW \) calculations, e.g., Alford et al.\(^{34}\) predicted a \( \Gamma \) gap of 0.2–0.3 eV for \( \text{YH}_3 \) and 0.8–0.9 eV for \( \text{LaH}_3 \), and Chang et al.\(^{35}\) obtained 0.8 eV for \( \text{LaH}_3 \). We found that the hexagonal and cubic \( \text{YH}_3 \) have similar small gaps, suggesting that the insulating properties are of electronic origin rather than structural.

Another interesting feature of the WDA band structures is that compared with the LDA, the overall valence bandwidth hardly changes. It supports a view that rare earth hydrides are not strong correlated systems. This is consistent with previous \( GW \) calculations,\(^{17,19,34}\) but in contrast to the many-body model Hamiltonian calculations which show a large valence bandwidth decrease.\(^{15}\) Thus, our results support the previous conclusion\(^{17,34}\) that rare-earth trihydrides are just band insulators, and that strong correlations are not required.

Although our DFT-WDA band gaps of \( \text{YH}_3 \) and \( \text{LaH}_3 \) agree with \( GW \) quasiparticle calculations very well, the measured optical gap is \( \sim 2.8 \) eV for \( \text{YH}_3 \) and \( \sim 1.8 \) eV for \( \text{LaH}_3 \), which are still 1–2 eV larger. Gelderen et al.\(^{17}\) argued that the fundamental band gap of hexagonal \( \text{YH}_3 \) is not the measured optical gap due to the forbidden transition between the highest valence and the lowest conduction bands. They concluded that the measured value corresponds to the direct gap at \( \Gamma \) of the hexagonal \( \text{LaF}_3 \) structure. However the real hexagonal \( \text{YH}_3 \) is more complex and it may have low symmetry so that the dipole matrix element could may well not be zero. Our DFT-WDA method may underestimate band gaps due to the DFT gap discontinuity at the Fermi level.\(^{36}\)

**IV. SUMMARY**

In conclusion, we have studied the band structures of the hexagonal \( \text{YH}_3 \) and cubic \( \text{YH}_3 \) and \( \text{LaH}_3 \) using the first-principles WDA method. The calculations showed that \( \text{YH}_3 \) and \( \text{LaH}_3 \) are both semiconductors, and this insulating property does not rely on the detailed crystal structure. The calculated band gaps agree with \( GW \) results very well, and they are also consistent with experiment. Our WDA calculations predicted good ground-state structures as well. The success of WDA may be attributed to the absence of self-interaction in \( 1s \) states.

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**APPENDIX: XC POTENTIAL OF THE WDA**

The xc potential \( V^{xc}(\mathbf{r}) \) in the DFT is the functional derivative of the xc energy,

\[
V^{xc}(\mathbf{r}) = \frac{\delta E^{xc}[\mathbf{n}] }{\delta n(\mathbf{r})}.
\]

In the shell-partitioning scheme as described in Sec. II, the xc potential of core states

\[
V^{xc}_{\text{core}}(\mathbf{r}) = \frac{\delta E^{xc}[\mathbf{n}] }{\delta n_{\text{c}}(\mathbf{r})} = V^{\text{LDA}}_{\text{xc}}(\mathbf{r}) + V_{1}(\mathbf{r}) - V_{2}(\mathbf{r}),
\]

where the first term is the ordinary LDA potential, and

\[
V_{1}(\mathbf{r}) = \int n_{\text{c}}(\mathbf{r}) n_{\text{c}}(\mathbf{r}') \frac{\delta G[\mathbf{r}-\mathbf{r}'|\mathbf{n}(\mathbf{r})]}{\delta n_{\text{c}}(\mathbf{r})} d\mathbf{r}'.
\]
In order to evaluate $V_3(r)$, we need the expression for $\tilde{n}(r)/\tilde{n}_v(r)$. This can be done by considering the variation of sum rule Eq. (7) with respect to $n_v(r)$,

$$\frac{\delta \tilde{n}(r)}{\delta n_v(r)} = \frac{n_v(r)}{n^2(r)} \int \frac{\delta G[|r'-r'|,\tilde{n}(r)]}{\delta \tilde{n}(r)} d\mathbf{r}'.$$  

If we denote $h_1(r)$ and $h_2(r)$ as

$$h_1(r) = \int \frac{n_v(r')}{|r'-r'|} \frac{\delta G[|r'-r'|,\tilde{n}(r)]}{\delta \tilde{n}(r)} d\mathbf{r}'$$

and

$$h_2(r) = \int n_v(r') \frac{\delta G[|r'-r'|,\tilde{n}(r)]}{\delta \tilde{n}(r)} d\mathbf{r'},$$

we can simplify

$$V_1(r) = \frac{n^2_v(r)}{n^2(r)} h_1(r).$$  

Similarly the xc potential of valence states is

$$V_{xc}^{\tilde{n}}(r) = \frac{\delta E_{xc}^{\tilde{n}}}{\delta n_v(r)} = V_{xc}^{\text{LDA}}(r) + V_3(r) + V_4(r) + V_5(r) + V_6(r) + V_7(r),$$

where

$$V_3(r) = \int \frac{n_v(r')}{|r'-r'|} G[|r'-r'|,\tilde{n}(r')] d\mathbf{r'},$$

$$V_4(r) = \int n_v(r') \frac{\delta G[|r'-r'|,\tilde{n}(r')] \delta G[|r'-r'|,\tilde{n}(r)]}{\delta n_v(r)} d\mathbf{r}'$$

and

$$V_5(r) = \int n_v(r') \frac{\delta G[|r'-r'|,\tilde{n}(r')] \delta G[|r'-r'|,\tilde{n}(r)]}{\delta n_v(r)} d\mathbf{r}'$$

$$V_6(r) = -\frac{n_v(r)n_v(r')}{n^2(r)} \frac{h_1(r)}{n^2(r)} h_2(r).$$