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Electronic structure of calcium hexaboride within the weighted density approximation

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We report calculations of the electronic structure of CaB_6 using the weighted density approximation (WDA) to density-functional theory. We find a semiconducting band structure with a sizable gap, in contrast to local-density approximation (LDA) results, but in accord with recent experimental data. In particular, we find an X-point band gap of 0.8 eV. The WDA correction of the LDA error in describing the electronic structure of CaB_6 is discussed in terms of the orbital character of the bands and the better cancellation of self-interactions within the WDA.

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The discovery of ferromagnetism in the lightly doped CaB_6 and SrB_6 resulted in considerable experimental and theoretical work aimed at understanding this unexpected phenomenon. The reported ferromagnetism is particularly remarkable considering that the material, $Ca_{1-x}La_xB_6$, contains no elements with partially filled d or f orbitals, and even more strangely, the ferromagnetism is associated with very low doping levels ($<1\%$), and therefore low carrier concentrations, has a very low moment ($\sim 0.07\ \mu_B$/La for $x = 0.005$), but a very high Curie temperature, T_C as high as 600 K (Ref. 1). Further, a semiconducting material, with ferromagnetism of this type, could potentially be of importance in producing room-temperature spintronic devices.[2,3]

Two different classes of theories were advanced early on in an effort to explain the strange ferromagnetism. The first was based on the doping of an excitonic or like system, i.e., an unconventional state in the parent, CaB_6,[4–7] and the second was based on the ferromagnetic phase of the dilute electron gas.[1,8,9] In the first class, the ferromagnetism arises from La induced doping of carriers into an excitonic ground state. This depends on a bare band structure that is semimetallic or very close to it, so that the prerequisite instability of CaB_6 to an excitonic state can exist. The second class mentioned does not depend on such an electronic structure, but rather involves a ferromagnetic instability of a low-density electron gas, though this class of theories suffers from difficulties obtaining the very high reported values of T_C. More pedestrian explanations for the observed ferromagnetism involving defects and their interactions and also extrinsic effects have been advanced more recently.[10–13]

This naturally resulted in a strong interest in the electronic structure of the parent compound CaB_6. First-principles calculations within the local-density approximation (LDA) predicted that CaB_6 and SrB_6 are semimetals with a small overlap at X point of the simple cubic Brillouin zone, or very small gap insulators,[14,15] consistent with the excitonic theories being formulated at that time. However, it is well known that the LDA often underestimates band gaps, and in some extreme cases it can predict a semimetallic band structure for a semiconductor, one example being Ge.[16] In simple semiconductors, the LDA underestimates of the band gaps are understood as being associated with an extreme nonanalytic and nonlocal behavior of density-functional theory as the particle number is changed to include a single conduction electron,[17,18] implying the need for a self-energy correction, or at least an orbital dependent potential to obtain a realistic description of band gaps.

The many-body quasiparticle GW approximation[19] is very successful in describing the band structures of insulators. In particular the self-energy correction implicit in it corrects most of the band-gap errors in simple semiconductors and other materials as well.[20] However, its results for CaB_6 have differed depending on the formulation of GW being used. Pseudopotential based GW calculations[3] yielded a sizable 0.8 eV band gap at X point, while recent all-electron GW results[21] showed an unexpected increase in band overlap relative to the LDA, perhaps related to the treatment of deep-core states.[22,23]

The electronic structure of CaB_6 has also been the subject of some debate from an experimental point of view, although a semiconducting electronic structure has become more generally accepted now. de Haas–van Alphen (dHvA) (Refs. 24 and 25) and Shubnikov de Hass (SdH) (Ref. 26) experiments were consistent with a semimetallic nature, while recent angle-resolved photoemission spectroscopy and resonant inelastic x-ray scattering measurements imply that CaB_6 is a semiconductor with a 1.0 (Ref. 27)–1.15 (Ref. 28) eV band gap. Recently, Rhyee *et al.* reported transport, optical, and tunneling measurements all consistent with a 1.0 eV band gap for pure CaB_6. They argued that the previously measured semimetallic characteristics in CaB_6, SrB_6, and EuB_6 actually originate from boron vacancies.[29]

We note that, as pointed out by Rodriguez and co-workers,[15,30] the valence and conduction bands of CaB_6 and the related hexaborides are of very different character, namely, B p valence bands and Ca derived conduction bands. This is reminiscent of the situation in the rare-earth trihydrides, e.g., YH_3. Those materials feature a semiconducting ground state, which is, however, predicted to be metallic in the LDA due to a band overlap between nominally occupied H derived states and nominally unoccupied metal states. In YH_3, this error is understood to be due to incomplete cancellation of self-interaction errors on the H sites in the LDA. These self-interactions lead to a H band position that is too high relative to the conduction bands, which is at least partly corrected in GW calculations.[31–33] It should be noted though

TABLE I. Theoretical and experimental lattice constant a (Å) and internal parameter x for CaB$_6$. The results denoted LAPW (PW) were from the LAPW (plane-wave) calculations.

	LDA (PW)	LDA (LAPW)	GGA (LAPW)	WDA (PW)	Experiment
a	4.08	4.09	4.15	4.13	4.15
x	0.201	0.202	0.202	0.206	0.207

that such self-interactions are a local effect, more akin in some ways to the on-site Coulomb effects that lead to Mott insulating states in transition-metal oxides, than to the nonlocal, nonanalytic discontinuities in density-functional theory that are important in simple semiconductors.[34] As such, the rare-earth trihydrides and perhaps CaB$_6$ are interesting test cases for theories of correlated electron systems, including density-functional based approaches.

Here, we present results of first-principles calculations based on the density-functional theory (DFT) within a nonlocal density approximation, namely, the weighted density approximation (WDA).[35–38] The WDA uses a model pair-distribution function to incorporate nonlocal information about the charge density into the exchange-correlation energy and potential, via an exact expression for the total energy. Unlike GW and like approaches, the WDA is oriented towards total energies rather than excitation spectra. As such, not surprisingly, it improves ground state properties, such as lattice parameters, relative to the LDA. Like the LDA, the WDA is exact for the total energy of the uniform electron gas, but unlike the LDA it is also exact for single-electron systems, where it is self-interaction free. We emphasize that the WDA is a smooth nonpathalogical approximation to density-functional theory, with only short-range nonlocality. It should be mentioned that the nonlocality of the self energy in the GW approach is mostly short range. The WDA exchange-correlation potential is a standard orbital independent (for valence states) potential, which different orbitals feel differently only through differences in the spatial distributions of their charge densities. It does not include the discontinuities that are present in the exact density-functional theory and are responsible for most of the band-gap correction in simple semiconductors such as Si. Detailed calculations for YH$_3$ and LaH$_3$ have shown that the WDA can yield insulating gaps of similar magnitude to the GW approximation in these hydrides due to the better cancellation of self-interaction errors, while at the same time improving the quality of ground-state properties.[39]

In the WDA the exchange-correlation (xc) energy expression is very similar to the general DFT form,

$$E_{\rm xc}^{\rm WDA}[n]=\int\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}G[|\mathbf{r}-\mathbf{r}'|,\overline{n}(\mathbf{r})]d\mathbf{r}d\mathbf{r}',\quad (1)$$

where G is the approximate model coupling constant averaged pair-distribution function, and $\overline{n}(\mathbf{r})$ is the weighted density which can be determined from the sum rule which states that the charge density in the exchange-correlation hole is unity.

$$\int n(\mathbf{r}')G[|\mathbf{r}-\mathbf{r}'|,\overline{n}(\mathbf{r})]d\mathbf{r}'=-1.\quad (2)$$

The WDA is exact for both a one-electron system and the uniform electron gas, independent of the model G used, provided that it is monotonic and properly normalized. Because the exact G function is not known, different forms of G have been tried,[40] from which we chose the following one:

$$G(r,n)=c\left\{1-\exp\left(-\left[\frac{r}{\lambda}\right]^{-4}\right)\right\},\quad (3)$$

This choice yields good energetics (structural properties) and band structures for the rare-earth trihydrides.[39] This type of G was derived from the Gunnarsson-Jones[41] ansatz, but it has a shorter range than the original one. Details of the WDA formalism used in this Brief Report can be found in Refs. 39 and 42.

The calculations were done using a plane-wave basis with pseudopotentials. The **k** grids for the Brillouin zone samplings during iteration to self-consistency were as dense as $12\times12\times12$, and the energy cutoff was 121 Ry.[43] The Ca semicore states were treated as valence states for the purpose of constructing Troullier-Martins pseudopotentials. Shell partitioning was employed as discussed in Ref. 38. We also did calculations with the linearized augmented plane-wave method (LAPW) (Ref. 44) using the LDA and the generalized gradient approximation (GGA) of Perdew and co-workers.[45] The LAPW LDA results agreed well with the plane-wave calculations.

The crystallographic structure of CaB$_6$ is simple cubic, with Ca atoms located at cubic corners. The B atoms form octahedral cages around the cube center. The internal parameter x determines the distance between a B atom and the cubic center. When $x=0.207$, the intraoctahedral and interoctahedral B-B distances are equal. Our calculated lattice constant a and internal parameter x within the LDA and WDA are shown in Table I along with LAPW LDA and GGA values. The WDA results are in excellent agreement with experimental data, while the LDA predicts a lattice constant 1.6% smaller, which is a typical LDA tendency. Thus, reflecting its origins in density functional theory, where energy and density are primary variables, the WDA improves upon the LDA structure. The GGA, like the WDA, predicts a lattice parameter in excellent agreement with experiment, but the band gap is small.

To facilitate comparison of the LDA and WDA electronic band structures, we used the experimental values of a and x for both the LDA and WDA. Figure 1 shows our results for the band structures of CaB$_6$. The LDA (left panel) predicts a tiny band gap (slightly more than 0.1 eV) at the X point,

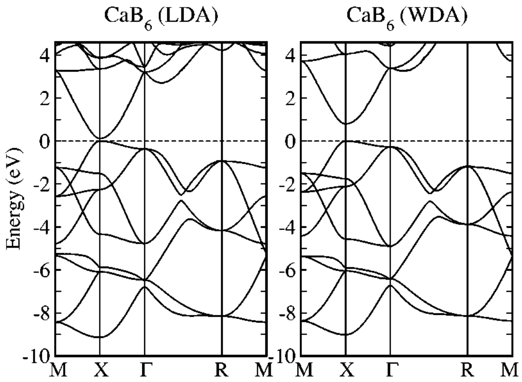

FIG. 1. Electronic band structure of CaB_6 within the LDA and WDA.

which agrees with Ref. 21, while other LDA results show a tiny overlap.[3,14,15] This small difference in band structure is due to different choices of the LDA scheme, chemistry (Sr vs Ca) and lattice structure as well as the approximations in using pseudopotentials. To check this we did well converged general potential LAPW calculations within the LDA for two structures. The first is the same experimental structure as used for Fig. 1, and the second is a structure where we relaxed the internal coordinate x in the LDA keeping the lattice parameter fixed at the experimental value. This yielded $x = 0.2025$. With the experimental value of $x = 0.207$ the LAPW calculations yielded a small band gap of 0.2 eV, while at $x = 0.2025$ a semimetal with a 0.1 eV band overlap is predicted. This implies that the structure is the key ingredient in reconciling the various results and also gives an error estimate of ~ 0.1 eV for our pseudopotential calculations. On the other hand, the right panel shows that within the WDA, the bands are shifted, quite similar to the cases of YH_3 and LaH_3, resulting in a sizable band gap of 0.8 eV at X point. The calculated GGA band gap is only 0.19 eV. Parallel WDA calculations using the uniform electron gas G function also yield a gap opening, though by a smaller amount. The band gap in that case is 0.3 eV.

Thus the WDA, with an appropriate choice of G, predicts CaB_6 to be a semiconductor with a gap comparable to that found in standard GW calculations[3] and in experimental spectroscopic measurements.[27–29] This shows that there exists a physical approximation to density-functional theory that is continuous and has only short-range nonlocality and that gives both a reasonable band-gap and ground-state properties (crystal structure) in agreement with experiment for CaB_6. We expect that WDA calculations would yield band-gap opening in SrB_6 as well.

In summary, WDA calculations predict that CaB_6 is a semiconductor, and the calculated band gap is in excellent agreement with recent experiments and quasiparticle GW calculations. Thus the WDA improves both the structural properties and electronic structure of these hexaborides, implying that the main error in the LDA description is associated with local self-interaction effects on B rather than the neglect of the nonanalytic discontinuity in density-functional theory across the band gap.

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