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GW quasiparticle corrections to the LDA+*U*/GGA+*U* electronic structure of bcc hydrogen

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In this paper, we study the quasiparticle electronic structure of atomic hydrogen in the body-centered cubic structure for various densities. We employ the *GW* approach to compute the electron self energy. For this model system, we use the local density approximation (LDA)+*U*/generalized gradient approximation (GGA)+*U* method as the mean-field solution starting point, which is known to work better than LDA/GGA for systems with strongly correlated electrons. In the low-density insulating phase, we find that the calculated *GW* quasiparticle gap is quite insensitive to the value of the on-site repulsive *U* employed over a wide range of physically reasonable values. Moreover, our result for the electronic gap agrees with the measured difference between ionization energy and electron affinity in the atomic limit.

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I. INTRODUCTION

Density functional theory (DFT) within the local spin density (LSDA) and generalized gradient (GGA) approximations provides accurate results for the ground-state properties of a broad spectrum of physical systems.[1] However, the method fails to describe properties of systems with strongly correlated electrons, such as those containing transition metal or rare earth atoms. In particular, as in semiconductors,[2] the electronic band gaps for the transition metal oxides are significantly underestimated and in some cases completely disappear.[3,4] The reason for this failure is that the Kohn–Sham eigenvalues in DFT do not physically correspond to quasiparticle excitation energies.[5]

One approximate method proposed to address this discrepancy is the local density approximation (LDA)+*U* method.[6–9] The introduction of a Hubbard-like *U* term in the exchange-correlation functional for the localized orbitals increases the degree of localization of the single particle wave functions and leads to the augmentation of the electronic gap and the formation of upper and lower Hubbard bands.

Another method widely applied in the study of the quasiparticle excitation properties of materials is the calculation of the electron self-energy within the *GW* approximation.[2,10] The eigenvalue equation that gives the quasiparticle energies and wave functions is formally written as

$$(T + V_{ext} + V_H + \Sigma)\psi = E\psi,$$

where T is the kinetic energy operator, V_{ext} is the external potential, V_H is the Hartree potential, and Σ is the self-energy operator. In general, Σ is a non-Hermitian, nonlocal, and energy-dependent operator and its exact calculation is formidable for real materials. Within the *GW* formalism, however, if we stop at the first term in the diagrammatic expansion with respect to the screened Coulomb interaction, this operator can be approximated by $\Sigma \approx iGW$, where G is the dressed Green's function and W is the screened Coulomb interaction. The calculation of the quasiparticle spectrum then may be proceeded by a rearrangement of the terms in the above equation with V_{xc} a chosen mean field,

$$[(T + V_{ext} + V_H + V_{xc}) + (\Sigma - V_{xc})]\psi = E\psi.$$

The expression containing the terms in the first set of parentheses is usually solved within DFT using either the exchange-correlation functional of LDA or GGA as the mean field, and the term $\Sigma - V_{xc}$ is then treated as a perturbation. This method has been widely applied to a range of systems and the results obtained are in excellent agreement with experiment.[2] In general, the *GW* method as practised, being a perturbative technique, works best when the mean-field solution is already close to the correct answer. For systems with strongly localized electrons, however, this may not be the case if LDA or GGA are used. Although good results have been obtained for some *d* and *f* electron systems,[11–15] the method is not guaranteed to work when the mean field solution qualitatively fails in describing the quasiparticle bands. The LDA+*U* method, on the other hand, should provide a better mean-field description for these systems and hence a more accurate starting point for perturbative *GW* calculations.

In this work, we combine the two methods, *GW* with LDA+*U*, to perform calculations on solid hydrogen in the body-centered cubic crystal structure. This particular system is chosen because it is a model system which has been extensively studied with techniques beyond simple DFT, and it exhibits a metal-insulator transition induced by correlation effects.

II. CALCULATION

The crystal structure of our model system, solid antiferromagnetic hydrogen in the body-centered cubic geometry, is given by a simple cubic lattice with two atoms of opposite spins per unit cell, one at the vertex and one at the body center of the cube. The lattice constant can be represented by the Wigner–Seitz parameter r_s, which is the radius of the sphere containing one electron. Since hydrogen has only one s localized valence orbital, the intra-atomic exchange parameter J in the LDA+*U* formalism is zero. We performed a series of DFT+*U* calculations for various values of the density and the *U* parameter using both LSDA (Ceperley–Alder

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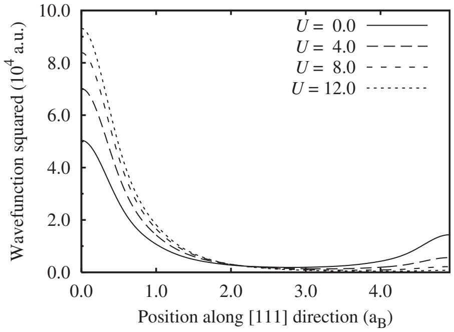

FIG. 1. $|\psi_\uparrow|^2$ for the valence band at Γ using LDA+U for $r_s = 2.8a_B$ and different values of U, plotted along the [111] direction. Solid curve: LDA result (U=0.0). Dashed curves: LDA+U for different values of U (in eV).

results[16] in the Perdew–Zunger parametrization[17]) and GGA (Perdew–Burke–Ernzerhof[18]) for the exchange-correlation functional. A Troullier–Martins pseudopotential[19] was used to describe the electron-proton interaction and a plane wave basis with a cutoff of 80 Ry was employed.[20] The value of the Monkhorst–Pack[21] grid spacing for each density was determined by converging the energy eigenvalues to better than 10^{-3} Ry. The orbital occupations of the LDA+U formalism were calculated by projecting the wave functions on normalized hydrogen 1s pseudoatomic orbitals. The random phase approximation was used for the calculation of the static dielectric function and the generalized plasmon pole model[2] was used for the extrapolation of the static dielectric function to finite frequency.

III. RESULTS

The dependence of the wave function shape on the U parameter for $r_s = 2.8a_B$ is shown in Fig. 1. The two ends of the x axis correspond to the positions of two nearest-neighbor hydrogen atoms (along the [111] direction) with opposite net local magnetic moments. As shown in the Fig. 1, the wave function becomes more localized for increasing values of U. It will be shown later that the LDA+U band gap linearly increases with respect to the U parameter. The widening of the band gap is due partly to the enhanced localization of the wave function, but mostly due to the presence of the U term in the Hamiltonian. Moreover, Fig. 1 shows that by increasing the value of U the majority spin population on each site increases, while the minority spin is suppressed. Therefore, the local net magnetic moment at each hydrogen site increases for larger U, and thus the antiferromagnetism is enhanced.

One of the GW/LDA+U quasiparticle band structures we obtained is shown in Fig. 2, which shows the opening of the band gap induced by the GW self-energy correction. We can see that the material is an indirect-gap insulator, the gap appearing between k-points R and X. This behavior was found for all densities and values of U for which the material is an insulator. Henceforth, the notion of the gap in this material refers to this indirect minimum gap.

The dependence of the gap on the U parameter is shown in Fig. 3. As anticipated, the Kohn–Sham gap for LDA+U and GGA+U monotonically increases with increasing U. Including GW corrections, we see that the behavior changes. For small values of U, the gap significantly opens up as expected. As U increases to physically expected values of 5–12 eV, however, the change in the GW gap is much smaller than that of the DFT+U calculation and approaches saturation at large U. The reason is that the exchange-correlation term V_{xc}, which explicitly contains U, has been subtracted from the quasiparticle eigenvalues. The dependence of the GW band gap on U primarily comes from the fact that the wave functions are more localized for the larger U and, to a lesser extent, to the U dependence of the dielectric properties. Inevitably, the two curves will cross for some value of U.

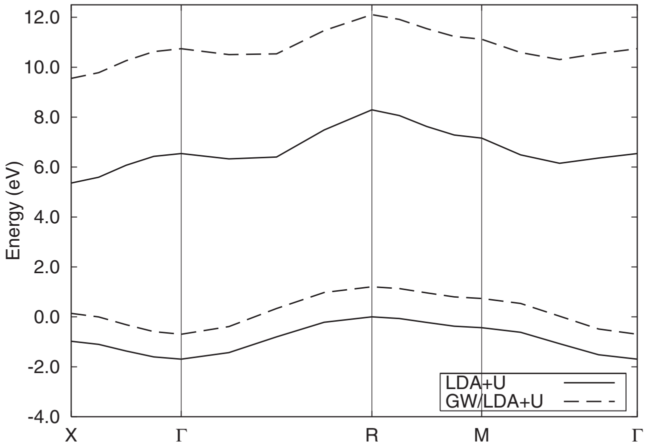

FIG. 2. The valence and conduction bands of solid bcc hydrogen calculated within LDA+U (solid line) and GW/LDA+U (dashed line) for $r_s = 3.3a_B$ and U=4.0 eV.

We would like to emphasize that this is an important and correct physical result. The GW results should be independent of the starting mean-field solution, provided the mean field solution is reasonably close to the final result so that perturbation theory is operative. Figure 3 illustrates this point very nicely. For U in the range of 5–12 eV, which is reasonable for hydrogen atoms in a low density environment, the final GW quasiparticle band is very insensitive to the starting

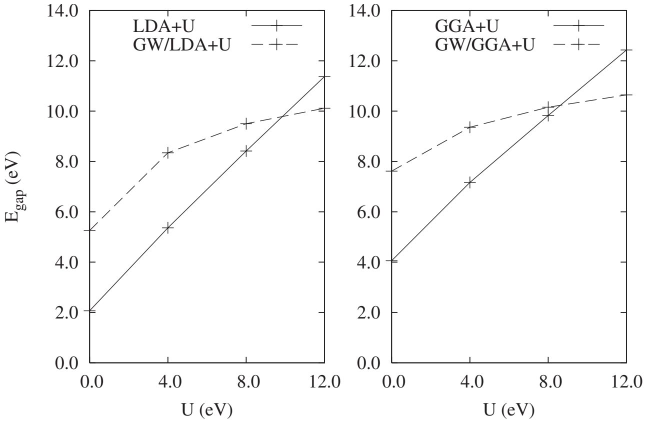

FIG. 3. The Kohn–Sham and quasiparticle gap versus the parameter U using mean field LDA+U (left) and GGA+U (right) for a density corresponding to $r_s = 3.3a_B$.

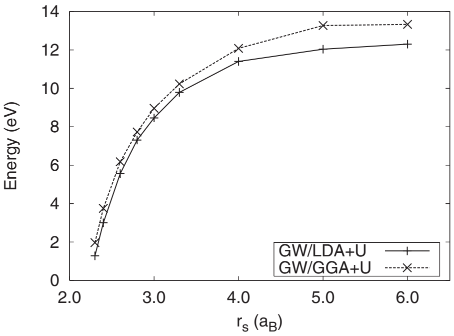

FIG. 4. The quasiparticle band gap versus the electron density parameter r_s.

mean-field gap (may it be either too small or large compared to the final result). We expect on physical grounds that the optimal result, with our theoretical framework, for the band gap is the value at where the two curves cross.

The magnitude of the quasiparticle gap for different densities is shown in Fig. 4 and the corresponding antiferromagnetic moment per site in Fig. 5. The gap should take on the atomic value in the low density limit, which is given by the difference between the ionization energy and the electron affinity of the hydrogen atom (Table I). As the density increases, the gap diminishes, and for some value of the density, it completely vanishes. By extrapolating our high density results, we find that the gap disappears at $r_s=2.24a_B$ for $GW/\text{LDA}+U$ and at $r_s=2.21a_B$ for $GW/\text{GGA}+U$. In Table I, we compare the critical density for the metal-insulator transition to results from previous studies, and we see that our calculations are in good agreement with variational quantum Monte Carlo calculations.[22] In the low density limit, we find that the $GW/\text{GGA}+U$ gaps are systematically larger than the $GW/\text{LDA}+U$ values, which is expected since in this density regime the wave functions are very localized and thus the gradient corrections are more significant. In the atomic limit, $GW/\text{LDA}+U$ slightly underestimates and $GW/\text{GGA}+U$ slightly overestimates the gap compared to experiment.

The dependence of the dielectric constant on the U parameter for $r_s=2.8a_B$ is plotted in Fig. 6(a). It is clear that the dielectric properties do depend on the value of U. Larger values of U increase the localization of the wave function and decrease the screening, thus increase the value of the electronic gap. In Fig. 6(b), the same data are shown, expressed in terms of the electronic gap averaged over the Brillouin zone. As seen in the figure, the data fall very close to the approximate expression $\epsilon_0=1+(\frac{\omega_p}{E_{\text{gap}}})^2$.

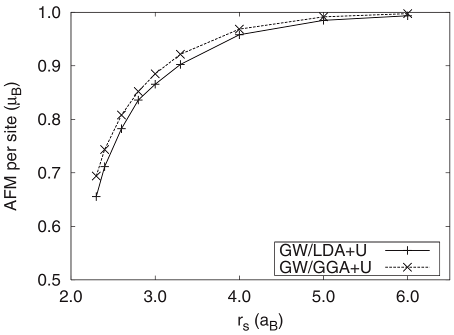

FIG. 5. The antiferromagnetic moment per site versus the electron density parameter r_s.

TABLE I. Wigner–Seitz radius r_s at the gap closure and the quasiparticle gap in the atomic limit computed with different methods.

Method	r_s at gap closure (a.u.)	E_g in atomic limit (eV)
$GW/\text{LDA}+U$	2.24	12.3
$GW/\text{GGA}+U$	2.21	13.3
VQMC[a]	2.20–2.30	
SIC-LSDA[b]	2.45	10.9
GW/LSDA[c]	2.65	10.8
GW/GGA[c]	2.42	12.6
Expt.[d]		12.8

[a] Reference 22.
[b] Reference 23.
[c] Reference 24.
[d] Reference 25.

IV. CONCLUSION

We use the GW approximation to include self-energy corrections in the LDA+U/GGA+U Kohn–Sham band structure of bcc solid hydrogen. We find that the value of the quasiparticle gap is very stable over a wide range of realistic values of U, extending from 5 eV (commonly used for transition metal oxides[26]) to 12.9 eV (atomic hydrogen[27]) with a variation of E_g of only $\sim 5\%$. Therefore, the method is very robust against the precise value of U. Moreover, the method predicts a metal-insulator transition at a density in agreement with variational quantum Monte Carlo results and gives an

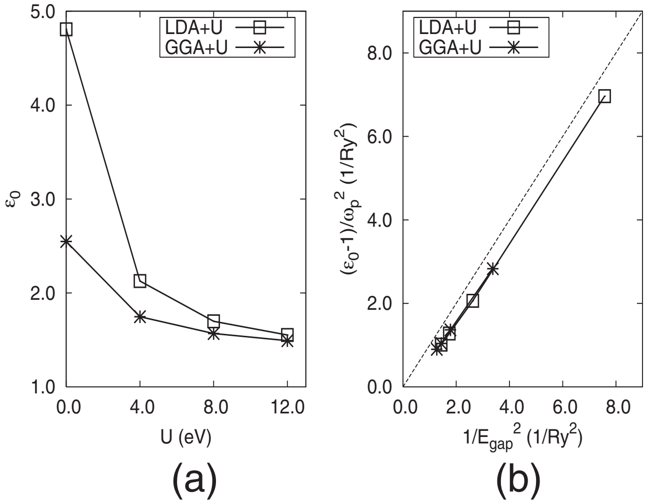

FIG. 6. (a) The dependence of the dielectric constant $\epsilon_0=1/\epsilon^{-1}_{\mathbf{G}=0,\mathbf{G}'=0}(q=0,\omega=0)$ on the U parameter for $r_s=2.8a_B$. (b) Plot of the expression $(\epsilon_0-1)/\omega_p^2$ versus the inverse of the average gap squared. The dashed line is the expression $y=x$.

accurate value for the gap at the atomic limit, as determined by experiment. In conclusion, we expect that starting from LDA+U/GGA+U using a reasonable value of U, one can apply GW corrections to systems with strongly correlated electrons to obtain significantly improved quasiparticle band structures.

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