Ab initio calculation of the quasiparticle spectrum and excitonic effects in Li$_2$O

Stefan Albrecht

Laboratoire des Solides Irradiés, URA 1380 CNRS-CEA/CEREM, École Polytechnique, F-91128 Palaiseau, France

Giovanni Onida

Istituto Nazionale di Fisica della Materia, Dipartimento di Fisica dell'Università di Roma Tor Vergata, Via della Ricerca Scientifica, I-00133 Rome, Italy

Lucia Reining

Laboratoire des Solides Irradiés, URA 1380 CNRS-CEA/CEREM, École Polytechnique, F-91128 Palaiseau, France

(Received 4 October 1996)

We report an *ab initio* calculation of the binding energies and the nature of the excitonic states in the near-gap absorption spectrum of a real solid, Li$_2$O. We calculate the ground-state properties using density-functional theory together with soft pseudopotentials. Applying Hedin's *GW* approximation for the self-energy corrections to the band structure, we determine the minimal gap about 1 eV above the measured absorption onset. Finally, we obtain agreement with experiment by solving an effective two-particle Schrödinger equation for the electron-hole pairs. [S0163-1829(97)00116-1]

Lithium oxide is a material of technological interest, with possible applications in deuterium-tritium fusion reactors as blanket breeding material[1] and in solid-state batteries.[2] Therefore, many experimental[3] and theoretical[4] studies are devoted to its defects, from the properties of simple point defects[4] to the formation of Li colloids under irradiation.[5] The electronic structure is needed to understand the results of many of the applied experimental techniques, such as optical absorption.[6–8] However, at present, calculations are essentially limited to Hartree-Fock investigations of the occupied valence states.[9]

Ab initio calculations, mostly density-functional theory– local-density approximation (DFT-LDA) applications, are currently performed for even complicated systems in order to determine the ground-state properties and the Kohn-Sham (KS) electronic structure.[10] However, it is well known that excited states, and hence the true electron addition and removal energies, are not correctly described by the KS eigenvalues. These energies should be obtained by using the true electron self-energy Σ (instead of the DFT-LDA exchange correlation potential) in an equation similar to the KS one. Using Hedin's *GW* approximation for Σ,[11] this self-energy correction to the KS band structure has been successfully evaluated for many materials;[12,13] the resulting quasiparticle (QP) energies, i.e., the electronic structure, are generally in excellent agreement with experiment. The calculations can be rather involved; in the case of oxides, the strongly attractive p component of the oxygen pseudopotential (PP) raises the necessity of a large plane-wave basis set. *GW* calculations on oxides can either be performed by applying further approximations or by introducing *soft* norm-conserving PP[14] for the oxygen, as done in Ref. 15. In the *ab initio* DFT-LDA framework, optical properties are usually calculated from one-electron transitions between KS states.[16] At this simple level, the computed absorption spectrum is not correct, since, e.g., the direct gap is generally wrong by 50% up to 100%. However, even when realistic QP energies are substituted for

the KS eigenvalues, there is no quantitative agreement between theory and experiment.[17]

In fact, these approaches still suffer from the neglect of many-body effects in the description of the absorption process: the interaction of the electron with the hole left behind in the valence state can be strong and lead to bound states and/or strong deformations of the spectrum. Up to now, these excitonic effects have only been rarely calculated for realistic systems, mostly in a semiempirical way,[18,19] or with an LDA-based self-consistent-field (ΔSCF) approach.[20] Recently, the inclusion of excitonic effects starting from the QP energies in the calculation of the absorption spectrum of a small sodium cluster[21] greatly improved the former rather poor agreement between calculated and experimental absorption spectra. The extension of this approach from a finite cluster to infinite solids is obviously of general interest.[22–24]

Our procedure starts with a DFT-LDA calculation of the ground-state properties and the KS electronic structure. We next determine the QP energies to obtain the occupied and empty bands of Li$_2$O. Finally, we calculate the optical transition energies, including excitonic effects. This calculation allows us to analyze in detail the nature of the electronic excitations contributing to the results.

Lithium oxide has antifluorite structure and can be described by a fcc cell with one oxygen and two lithium atoms. We have determined the ground state properties within the DFT-LDA pseudopotential-based Car-Parrinello method.[25] We used the Martins-Troullier (MT) PP generation scheme[14] to reduce the number of plane waves needed. We have first applied the relatively smooth MT PP for oxygen described in Ref. 26. This potential achieved convergence with a plane-wave cutoff of 80 Ry. To further reduce the computational effort we have investigated a smooth version[15] with cutoff radii r_c=2.30 a.u. for the s component and 1.95 a.u. for the local p component ($s\underline{p}$). In this case, the required cutoff energy is 50 Ry. For the lithium atom we chose a MT PP with r_c=1.75 a.u. for both the local s as well as the p com-
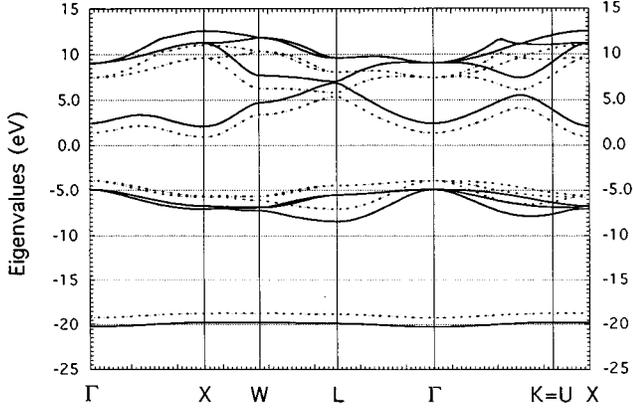
FIG. 1. QP (full lines) and DFT-LDA (dashed lines) band structure of Li_2O for the valence and the first unoccupied bands. The top of the LDA valence bands at Γ is set at -3.9 eV.

ponent (sp), the latter one created from a slightly excited atomic configuration. Using two special $\mathbf{k}$ points,[27] we obtained good agreement with experiment[28] for the lattice constant and the bulk modulus (calculation: $a_0 = 4.534$ Å; $B = 0.90$ Mbar; experimental: $a_0 = 4.573$ Å, $B = 0.90$ Mbar) with both PP configurations. Characteristically for a strongly ionic bond, the valence charge is almost entirely concentrated around the oxygen atom.

Although the Kohn-Sham LDA eigenvalues were converged to better than 10 meV for the two PP configurations, we found that with the low cutoff one the gap is slightly overestimated (about 0.15 eV). This error can be tolerated: the minimum LDA gap is direct, at the Γ point, and as large as 5.3 eV. As expected, the LDA gap underestimates the value of the onset of optical absorption, found experimentally at about 6.6 eV.[7] The dashed lines in Fig. 1 show our results for the LDA band structure. The occupied bands are due mostly to oxygen ($2s,2p$) and are very flat. The lowest unoccupied band is also mostly localized on the oxygen atoms and is very flat along the $\overline{\Gamma X}$ direction, consistent with the geometry of the underlying oxygen sublattice.

The LDA eigenvalues and eigenfunctions are then used as input to the evaluation of the random-phase-approximation screened Coulomb interaction, W, and the GW self-energy Σ. Every matrix element of $W_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega)$ is calculated at two imaginary energies, and the energy dependence is fitted to a plasmon-pole model along the imaginary energy axis.[29] We evaluate the QP energies in first-order perturbation theory in $\Sigma - V_{xc}$.[12,13]

Using ten special $\mathbf{k}$ points the GW corrections open the gap at the Γ point by 2.1 eV, yielding a minimum direct gap of 7.4 eV. Comparison of the corrections shows that shifts are identical to within 30 meV for both pseudopotentials, as expected from a first-order perturbation correction. Roughly, the unoccupied bands are shifted down and the occupied ones are shifted up by about 1 eV in either case (Fig. 1). The band dispersion is only slightly modified, up to 0.40 eV. In spite of the well-established reliability of *ab initio GW* calculations, we have hence found a QP gap that differs by almost 1 eV from the measured ''optical gap''.[30] However, screening in Li_2O is weak: as a byproduct of the GW calculation, we obtain the macroscopic dielectric constant ε_0, which is 3.5 for both PP configurations.[31] This fact, together

with the small dispersion of the top valence and bottom conduction bands, suggests that the electron-hole interaction should be large, which would lead to optical transitions at energies well below the QP gap.

Following the approach of Ref. 21, we compute the binding energies of the excitons from a two-particle effective equation derived from Green's-function theory.[22–24] Unlike for a finite system, band dispersion has to be taken into account here. We limit ourselves to the case of zero momentum excitons, i.e., direct transitions with $\mathbf{k}_\nu = \mathbf{k}_c = \mathbf{k}$ and, as in Ref. 21, neglect dynamical effects, namely the energy dependence of the inverse dielectric matrix $\varepsilon_{\mathbf{GG}'}^{-1}(\mathbf{q},\omega)$ in the Coulomb interaction.[23] This approximation is well justified, since the exciton binding energies turn out to be much smaller than the band gap. Then the equation, which includes the screened electron-hole interaction as well as the unscreened electron-hole exchange term, reads in momentum space as

$$(E_{c\mathbf{k}} - E_{\nu\mathbf{k}})A^{c\nu\mathbf{k}} + \frac{4\pi}{\Omega}\sum_{\mathbf{k}'}\sum_{c'\nu'}\left\{2\sum_{\mathbf{G}}\frac{1}{|\mathbf{G}|^2}\langle c\mathbf{k}|e^{i\mathbf{G}\cdot\mathbf{r}_1}|\nu\mathbf{k}\rangle\right.$$
$$\times\langle\nu'\mathbf{k}'|e^{-i\mathbf{G}\cdot\mathbf{r}_2}|c'\mathbf{k}'\rangle$$
$$-\sum_{\mathbf{GG}'}\frac{\varepsilon_{\mathbf{GG}'}^{-1}(\mathbf{q})}{|\mathbf{q}+\mathbf{G}'|^2}\langle c\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}_1}|c'\mathbf{k}'\rangle$$
$$\left.\times\langle\nu'\mathbf{k}'|e^{-i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}_2}|\nu\mathbf{k}\rangle\delta_{\mathbf{q},\mathbf{k}-\mathbf{k}'}\right\}A^{c'\nu'\mathbf{k}'} = \varepsilon A^{c\nu\mathbf{k}}. \quad (1)$$

Local-field effects are considered in ε^{-1} taken from the GW calculations. The one-particle energy levels $E_{\mu\mathbf{k}}$ are identified with the QP energies. The basis set for the exciton states is given by the products of the calculated occupied and empty LDA states $|\mu\mathbf{k}\rangle$. The exciton eigenstate is then described by

$$|N^*\rangle = \sum_{\mathbf{k}}\sum_{c\nu}A^{c\nu\mathbf{k}}c_{c\mathbf{k}}^+c_{\nu\mathbf{k}}|N\rangle, \quad (2)$$

where $|N\rangle$ is the ground state and $c_{n\mathbf{k}}^+$ creates an electron in the LDA state $|n\mathbf{k}\rangle$. This is consistent with the standard perturbative GW formulation, where the Green's function is constructed using the LDA eigenstates.

In the crystal, attention has to be paid to the limits of vanishing wave vectors in the exchange and Coulomb matrices. The divergence in the Coulomb term is integrated out over a small volume around $\mathbf{q} = \mathbf{0}$. In the exchange matrix, the $\mathbf{G} = \mathbf{0}$ contribution actually has to be understood as the limit $\mathbf{k}_\nu \to \mathbf{k}_c$, and gives a finite contribution that we evaluate in $\mathbf{k}\cdot\mathbf{p}$ perturbation theory. This limit is nonanalytical, which is at the origin of the transverse-longitudinal splitting for degenerate bands.[24]

Finally, we find the exciton eigenvalues and eigenfunctions by diagonalizing the effective Hamiltonian matrix. The explicit knowledge of the coupling of the various two-particle channels, given by the coefficients $A^{c\nu\mathbf{k}}$, allows us to identify the character of each transition. In order to obtain convergence (within 30 meV), we had to use 19 special $\mathbf{k}$ points in the irreducible Brillouin zone, eight bands, and about 300 plane waves. We find the lowest exciton eigenvalue at 6.6 eV for the two transverse transitions with a small

0.037 -----   0.0135 ·····   0.005 ·········

(a)

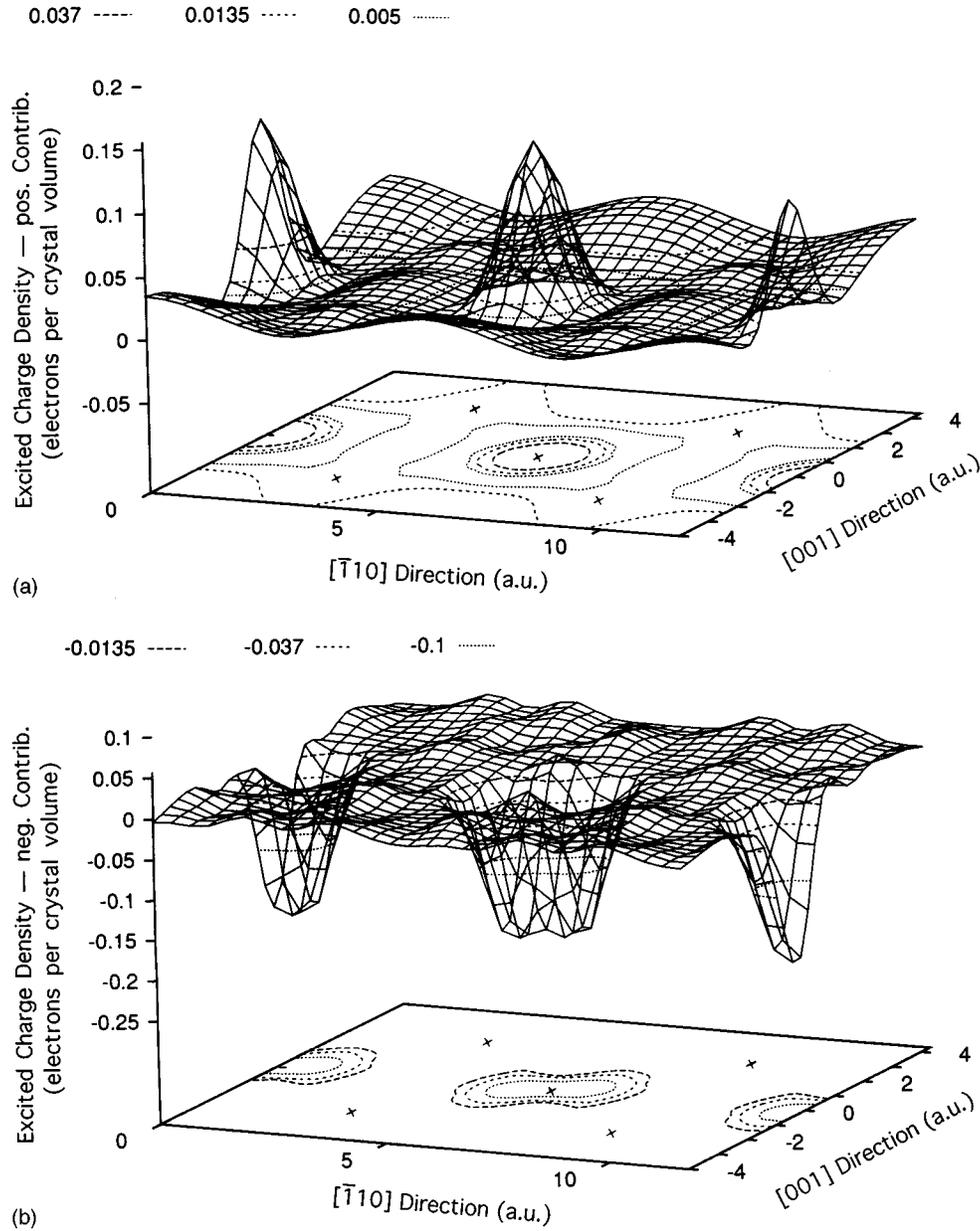-0.0135 -----   -0.037 ·····   -0.1 ·········

(b)

FIG. 2. Difference between the charge density in one of the two lowest excited states and the ground-state charge density in the (110) plane, in units of electrons per crystal volume. Panel (a): positive, (b): negative contributions. Crosses indicate Li and O atoms, with oxygen in the center. Distances in a.u.

split of about 50 meV to the longitudinal component; this value is of the order of the global precision of our calculations.[33] The dominant contribution comes from the transitions from the threefold degenerate $2p$ bands to the $3s$ band mostly due to the oxygen. The corresponding electric dipole transition is allowed. Thus, this lowest eigenvalue corresponds to the onset of the optical absorption, consistent with experiment.[7]

In Fig. 2 we visualize the infinitesimally small perturbation of the charge density caused by the electronic excitation by plotting the difference between the excited state density $\rho^*(\mathbf{r})$ and the ground-state density $\rho(\mathbf{r})$ as the number of electrons per crystal volume [whereas the density $\rho(\mathbf{r})$ is usually shown as the number of electrons per unit cell]. We obtain $\rho^*(\mathbf{r})$, in terms of the one-electron wave functions

$\psi_{n\mathbf{k}}(I)$, by evaluating the expectation value of the charge-density operator in the exciton eigenstate (2):

$$\rho^*(\mathbf{r}) - \rho(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{cv} \left(-\sum_{v'} A^{cv\mathbf{k}*} A^{cv'\mathbf{k}} \psi_{v\mathbf{k}}(\mathbf{r}) \psi^*_{v'\mathbf{k}}(\mathbf{r}) \right.$$
$$\left. + \sum_{c'} A^{cv\mathbf{k}*} A^{c'v\mathbf{k}} \psi^*_{c\mathbf{k}}(\mathbf{r}) \psi_{c'\mathbf{k}}(\mathbf{r}) \right). \qquad (3)$$

Panel (a) shows the positive and panel (b) the negative contributions for one of the two degenerate lowest excited states. The infinitesimal excited dipole is localized on the oxygen atom; the charge density of the electron is very similar to that of the LDA bottom conduction state.

The fact that transitions to or from other bands contribute little to the exciton state allows us to analyze our result from the point of view of the effective-mass approximation:[24] we can roughly fit our envelope function $A^{c\nu\mathbf{k}}$ to the hydrogen-like result $A(k)/A(k=0)=[1+(ka_{ex})^2]^{-2}$ in order to extract an estimate for the model exciton radius a_{ex}. We obtain a binding radius of about half the lattice constant, consistent with the large binding energy of the exciton.

It is also possible to analyze the higher transitions, using the $A^{c\nu\mathbf{k}}$ and the dipole matrix elements between the LDA states to compute the absorption spectrum. However, this would require a larger $\mathbf{k}$ point set in order to obtain the necessary precision, and is beyond the scope of the present work on the optical gap.

In summary, we have performed *ab initio* calculations of the ground-state properties of Li_2O, using efficient smooth pseudopotentials. Small imprecisions thereby introduced in the DFT-LDA eigenvalues are neither removed nor enhanced by the subsequently applied GW corrections, which mainly open the LDA gap without notably altering the dispersion. We have evaluated two-particle corrections by calculating the excitonic binding energies for zero momentum excitons at the same level of approximation as the QP corrections, though neglecting dynamical effects. The optical absorption onset was determined in agreement with experiment. Our approach allows us to study in detail the various two-particle channels contributing to each eigenstate, and enables us in principle to construct the complete absorption spectrum, including excitonic effects for a wide class of materials.

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