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All-Electron versus Pseudopotential Calculation of Optical Properties: The Case of GaAs

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Dedicated to Professor Dr. Wolfgang Richter on the occasion of his 60th birthday

The reliability of the widespread practice of calculating the optical properties of solids using pseudo wavefunctions instead of the true electron wavefunctions has been tested in the case of bulk GaAs. Pseudopotential calculations of the imaginary part of the dielectric function – where the matrix elements of the momentum operator are calculated between pseudo wavefunctions – have been compared with all-electron full-potential linear muffin-tin orbital calculations where the true wavefunctions are used. No evidence has been found of differences due to the different sets of wavefunctions employed in the two approaches.

1. Introduction

The optical properties of solids are routinely calculated within Density Functional Theory in the Local Density Approximation (DFT-LDA), by expanding the Kohn-Sham wave functions in plane waves, see e.g. [1]. This is made possible by the use of modern norm-conserving pseudopotentials, which allow to obtain highly accurate valence and conduction band energies and eigenstates without explicitly including the core electrons in the calculation. "Freezing" the core electrons is crucial when a plane-wave basis is used: the number of basis functions needed to describe the 1s orbital in a Si atom is in fact more than 1000 times larger than in the case of the valence shell. Since the inclusion of self-energy effects and electron–hole interaction is still computationally hard, see e.g. [2], the above scenario (DFT-LDA, pseudopotentials, and plane-wave expansion) is widely used at present. Recently this approach has been extended to the calculation of surface optical properties [3]. Here, one is interested in changes in the spectra of the order of 1% with respect to the bulk spectrum, or between spectra calculated for different light polarization.

The pseudopotential method ensures that the eigenvalues are the same as those of the all-electron problem; however, pseudo wavefunctions are different from the true wavefunctions inside the core radius, where the former ones are rather smooth, while the latter have narrow oscillations. The matrix elements of the optical transitions should be calculated, strictly speaking, between the true wave functions, not between pseudo wavefunctions. No theorem allows to use pseudo wavefunctions, the only rationale for their usage being the simplicity and the hope that the wrong representation of wavefunctions, being limited to within the (small) core radius, might be unimportant.

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Only a few studies have addressed this point so far. Kageshima and Shiraishi [4] have developed a method to 'repair' pseudo wavefunctions, by replacing them with the true atomic wavefunctions inside the core radius. They have calculated the momentum matrix elements for GaAs and GaN at some high-symmetry points, without obtaining a full spectrum: they found a small effect in GaAs, and a more relevant one in GaN. Shkrebtii et al. [5], on the other hand, calculated spectra for GaAs and GaP using both a pseudopotential and a full-potential linearized augmented plane-wave (FLAPW) approach. Similar spectra are obtained within the two approaches. Since, however, a scissors-operator shift was included in the FLAPW spectrum, but not in the pseudopotential spectrum, a quantitative comparison between them is not easy.

The purpose of this work is to make a thorough analysis of the error made using pseudo wavefunctions in the calculation of optical properties. We will compare the optical spectrum of GaAs calculated within the pseudopotential method with that obtained within the Full Potential-Linearized Muffin Tin Orbital (FP-LMTO) method.

Below we briefly describe the two methods, their computational ingredients and the resulting band structures. Finally, we will compare the optical spectra obtained within the two methods. They are very similar, with small discrepancies clearly related to discrepancies in band energies. Hence we conclude that using pseudo wavefunctions instead of all-electron wavefunctions does not introduce relevant errors in the optical spectrum, at least in the case of GaAs.

2. Calculational Details

Let us describe first the details of the pseudopotential method. Norm-conserving pseudopotentials (NCPP) have been generated within the Hamann scheme [6, 7], using the following set of cutoff radii: $R_s = 1.19$, $R_p = 1.22$, $R_d = 1.42$ atomic units for Ga, and $R_s = 1.40$, $R_p = 1.18$, $R_d = 2.28$ atomic units for As. Exchange-correlation has been accounted for within LDA using the exchange correlation potential calculated by Ceperley and Alder [8], in the analytic form given by Perdew and Zunger [9]. Nonlinear core corrections [10] have been included for Ga, and extensive transferability checks have been performed, both on logarithmic derivatives *and* by explicitly comparing pseudoatom and all-electron calculations for isolated Ga and As atoms in excited and/or partially ionized configurations. The nonlocal parts of the pseudopotentials have been treated within the Kleinman-Bylander scheme [11], taking the s (d) component as a reference local potential for Ga (As). The electronic structure of bulk GaAs has been calculated with a kinetic-energy cutoff of 18 Ry, at the theoretical lattice constant, $a = 10.56$ atomic units. The optical spectrum has been calculated within the velocity gauge, by computing the matrix elements of the momentum operator, without correction for the pseudopotential non-locality [1], at 50000 random points in the full Brillouin zone.

The all-electron calculation has been carried out self-consistently using the full-potential version [12] of the LMTO method [13] at the same value of the lattice constant and using the same exchange-correlation scheme as above. Again, the optical spectrum has been determined within the velocity gauge, by calculating the matrix elements of the momentum operator between muffin tin wavefunctions. The reciprocal space integration is performed with the analytical tetrahedron method [14] using 752 points in the irreducible wedge of the Brillouin zone.

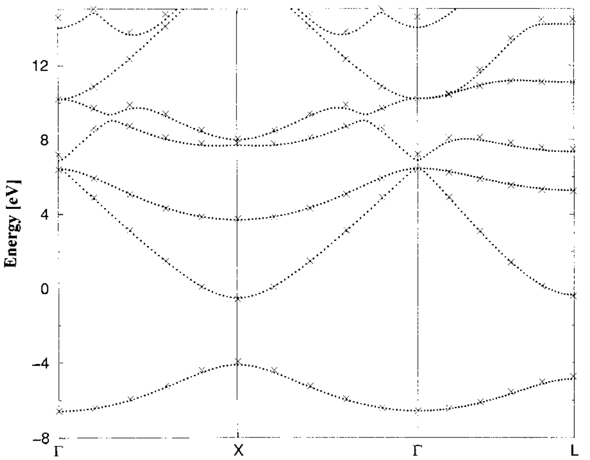

Fig. 1. Band structure of bulk GaAs calculated with the NCPP method (dotted curves), versus that calculated with FP-LMTO (crosses)

3. Results

The energy bands obtained using the two methods are shown in Fig. 1. The two band structures are very close to each other. The greatest difference, although hardly seen in Fig. 1, is that in the direct gap, which is 0.5 eV in the pseudopotential calculation and 1.1 eV in the LMTO calculation. It is well known that the direct gap of GaAs is very sensitive to the details of the calculation, as the value of the lattice constant, kinetic-energy cutoff, and relativistic effects [15]. Since all other ingredients are the same in the two calculations, the difference above may be probably ascribed to the incompleteness of the LMTO basis (low-cutoff plane-wave bases yield indeed higher gaps [15]).

The two optical spectra are shown on the same scale in Fig. 2. They are very similar, except near the absorption edge. This discrepancy is of course due to the different direct gaps obtained within the two approaches. The small intensity differences at higher energies are probably due to the different samplings of the Brillouin zone. We do not see any indication of differences arising from matrix-element errors due to an imperfect mimicking of wavefunctions by the pseudo wavefunctions.

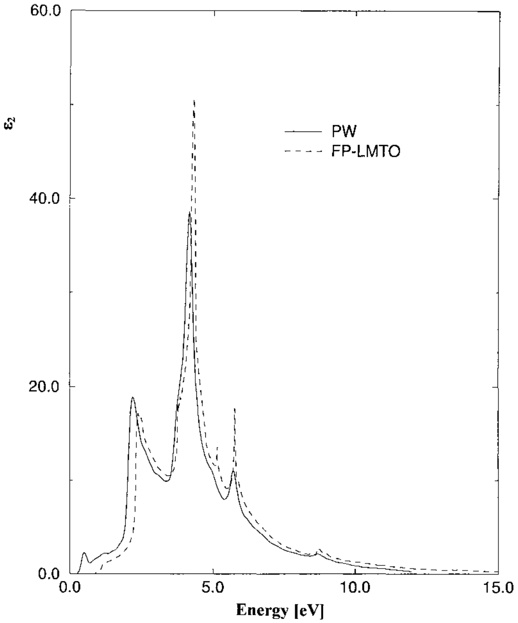

Fig. 2. Imaginary part of the dielectric function of GaAs versus photon energy. Full line: NCPP calculation, dashed line: FP-LMTO calculation

4. Conclusions

In conclusion, we have checked the reliability of using pseudo wavefunctions, as it is generally done, in the calculation of optical properties, by comparing pseudopotential with full potential LMTO calculations. We find that this does not induce visible mistakes in the optical spectrum of GaAs, in agreement with previous similar findings [4, 5]. However, this conclusion should not be taken as absolute, for two reasons: first, the fact that the LMTO basis, although fairly large, cannot be made complete in a straightforward way (see its overestimation of the direct gap of GaAs as a measure of its incompleteness); second, the agreement between pseudopotential and LMTO spectra may be worse in other materials. We have preliminary evidence that a greater difference is present in the case of copper.

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