Dynamical density response of II-VI semiconductors

A. Fleszar and W. Hanke
Institut für Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

(Received 12 June 1997)

We report results of *ab initio* calculations of the dynamical density response in CdTe, CdS, and CdSe. The calculated loss functions in all these semiconductors are rich in fine structures and show a rather unusual, negative dispersion of the loss peak due to the interaction of interband transitions with the plasmon. The detailed shape of the loss function in these compounds is strongly affected by various factors, such as the presence of occupied semicore Cd-4d states, the self-energy effects which shift down these states to the experimentally observed position, and electron-hole vertex corrections in screening. [S0163-1829(97)04443-3]

Linear response functions are useful and important quantities for many-electron systems. Of particular importance is the density-response function, directly connected to the density-density correlation and dielectric function. It describes electron-hole (e.g., optical) and collective electronic excitations, determines via the screening W single-particle excitations (e.g., in the GW approximation), and also accounts for the ground-state energy of a many-electron system.[1] Additionally, it determines the cross section for inelastic scattering of x rays or fast electrons.

Calculations of response functions from first principles for real materials are computationally extremely demanding. The main difficulty stems from the inclusion of the actual band structure of the material. Additional difficulty comes from a complicated interplay of nonlocality effects introduced by lattice potential and correlation effects, which in turn are usually enhanced by the strength of the crystal potential and electron localization. An interaction between electron-hole and collective excitations can cause strong deviations of the shape of response functions from the predictions of simple models and can necessitate a self-consistent calculation of the response properties of the system based on the actual band structure. It was realized recently that such problems are present even in the case of simple metals.[2–4] In the case of partially ionic II-VI semiconductors with their rather strong crystal potential and localized semicore cation d electrons, all these problems are very important and the calculation of response functions consists of a computational challenge.

In this paper we report on *ab initio* results for the dynamical density response of a series of II-VI semiconductors: CdTe, CdS, and CdSe. The II-VI semiconductors, due to their direct and rather large gap, are technologically important materials. The recent successful fabrication of the blue-green laser diode on the basis of these materials has renewed interest in their physical properties. Theoretically, they present interesting solids, in which partially covalently bound s-p electrons interact with more localized cation d electrons. The effect of this interaction on the ground-state properties in II-VI compounds was studied within the local-density approximation[5] (LDA) by Wei and Zunger.[6] The one-particle excitations, probed, for example, by the direct or inverse photoemission experiments, have been recently studied theoretically via the many-body GW approach with the explicit inclusion of the semicore cation d electrons.[7] In the present paper, we examine the two-particle excitation properties in this class of materials, which are probed in scattering experiments with fast external particles, e.g., x rays, or fast electrons. We find that in all semiconductors studied here, there exists a negatively dispersing loss structure. These findings are predictions in that we are not aware of any experimental determination of the loss dispersion in these materials. The calculated loss spectrum in these compounds is rich in fine structures and strongly depends on various factors, such as the inclusion of semicore Cd-4d states, self-energy corrections, and vertex corrections in the irreducible two-particle interaction.

In the framework of the time-dependent density-functional theory,[8,9] the density-response function $\chi(\mathbf{r},\mathbf{r}';\omega)$ can be expressed as

$$\chi=\chi^{(0)}[1-(v_c+f_{\mathrm{xc}})\chi^{(0)}]^{-1}, \qquad (1)$$

where $\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega)$ is the nonlocal and dynamical density response of *noninteracting* Kohn-Sham electrons, with $v_c(\mathbf{r},\mathbf{r}')=1/|\mathbf{r}-\mathbf{r}'|$. The quantity $f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';\omega)$ describes vertex corrections in the two-particle interaction, i.e., in the screening.[9,10] For simplicity, we have dropped the arguments $\mathbf{r},\mathbf{r}',\omega$ from Eq. (1). $\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega)$ is given by the standard expression in terms of the Kohn-Sham orbitals ψ_{kn} and energies E_{kn}:

$$\chi^{(0)}(\mathbf{r},\mathbf{r}';\omega)=\sum_{kn,k'n'}\frac{f_{kn}-f_{k'n'}}{E_{kn}-E_{k'n'}+\omega+i\eta}\times\psi^{*}_{kn}(\mathbf{r})\psi_{k'n'}(\mathbf{r})\psi^{*}_{k'n'}(\mathbf{r}')\psi_{kn}(\mathbf{r}'), \qquad (2)$$

where f_{kn} are the Fermi factors. In what follows, we use atomic units.

Equations (1) and (2) give an *exact* description of the dynamical response in the many-body system, provided the Kohn-Sham orbitals and energies were *exact* and the many-body vertex correction f_{xc} was known. However, both are unknown and a common practice is to use $\chi^{(0)}$ calculated within the local-density approximation and either to ignore the f_{xc} factor, which corresponds to the screening within the random-phase approximation (RPA) for Kohn-Sham electrons, or to express f_{xc} within one of the existing models, which usually are developed for the homogeneous electron gas case. Our approach follows this practice: we calculate $\chi^{(0)}$ from the LDA band structure, with the Ceperley and Alder exchange-correlation energy functional and potential.[11] *Ab initio* pseudopotentials are used including explicitly Cd-4d states.[12] The Bloch states are projected into a mixed basis consisting of localized functions centered at Cd sites and plane waves. We have assumed the zinc blende structure for all three compounds studied (with the lattice constant of 12.25, 11.02, and 11.50 a.u. for CdTe, CdS, and CdSe, respectively). While for CdTe the zinc blende structure is the natural phase, the other two materials crystalize in the wurzite structure. With the modern molecular-beam epitaxy technology, however, it is possible to produce thin samples with the zinc blende phase for CdS and CdSe as well.

The density-response function χ is connected through the relation $\epsilon^{-1}=1+v_c\chi$, with the inverse dielectric function. Both quantities can be Fourier transformed in momentum space, thus becoming matrices in the reciprocal lattice vectors $\vec{G}$ and $\vec{G}'$. The negative of the $\vec{G}=\vec{G}'=0$ element of the imaginary part of the ϵ^{-1} matrix is the *loss function.* Im $\chi_{\vec{G}=0,\vec{G}'=0}(\vec{q};\omega)$ is proportional to the dynamical structure factor of the system $S(\vec{q};\omega)$:

$$S(\vec{q};\omega)=-2\hbar\Omega\ \mathrm{Im}\ \chi_{\vec{G}=0,\vec{G}'=0}(\vec{q};\omega) \tag{3}$$

and describes the cross section for inelastic scattering of fast electrons or x rays. Ω is the crystal volume.

In Fig. 1 we show the dispersion of the loss function in CdTe, CdS, and CdSe, calculated within the RPA approximation for q between 0 and 0.4 a.u. along the (100) direction. In all three compounds the shape of the loss function is very different from the case of simple metals, where a single and very narrow plasmon line dominates the spectrum for small enough wave vectors. Even in the case of an element semiconductor like silicon, the loss function is significantly more peaked and plasmonlike. Here we observe several peaks and a rather broad spectrum. However, the most spectacular feature is the negatively dispersing peak around 12–13 eV. Similar to the negative plasmon dispersion in cesium,[3,4] we expect that also in the case of II-VI compounds the negative dispersion of the loss peak originates from the interaction of the collective excitation with interband transitions.

Let us analyze in more detail the case of CdTe. In order to exhibit the rate of excitations of interband transitions for Kohn-Sham electrons, we display in Fig. 2 the $\vec{G}=\vec{G}'=0$ element of the imaginary part of the $\epsilon(\vec{q}+\vec{G},\vec{q}+\vec{G}';\omega)$ matrix ($\epsilon=1-v_c\chi^{(0)}$) for growing $\vec{q}$ vectors in the energy region around main loss peaks. The shape of Im(ϵ) explains the mechanism of the negative dispersion: there is a dispersionless electron-hole peak in Im(ϵ) at ω between 12–13 eV, whose strength grows with growing $\vec{q}$ vector. As a consequence of this interband peak (which occurs in the region, where the real part of ϵ is small), the shape of the loss function is distorted. Therefore, for $q=0$, instead of a sharp loss peak, which would occur at about 13 eV,[13] a broader peak at 12.2 eV appears. The main loss structure in CdTe for $q=0$, which occurs at 14.2 eV and shows a positive dispersion, is to be traced back to the interaction of the plasmon with the interband peak in Im(ϵ) at ~15.5 eV.

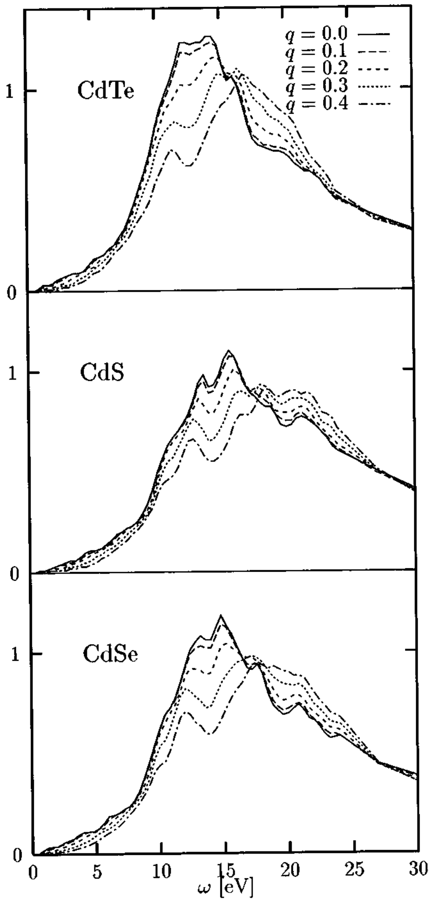

FIG. 1. The dispersion of the loss function of CdTe, CdS, and CdSe calculated within the RPA approximation for $\vec{q}$ vectors (in a.u.) along the (100) direction.

In order to analyze the origin of interband peaks in Im(ϵ), Fig. 3 plots the LDA band structure of CdTe along L-Γ-X directions. We have neglected the spin-orbit splittings in the band structure, which, although quite large in the case of CdTe, should not affect the shape of response functions in the energy range of 10–20 eV. A common feature of all

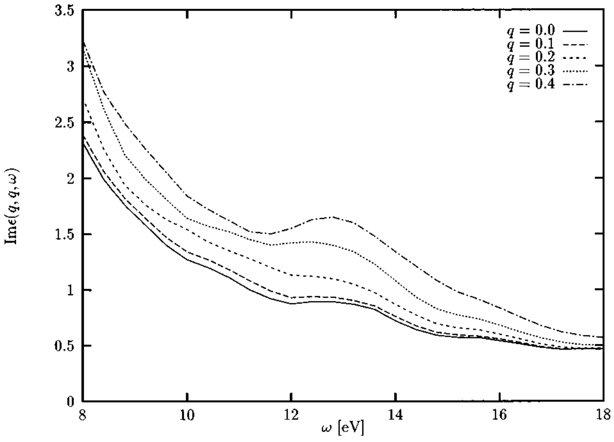

FIG. 2. The $\vec{G}=\vec{G}'=0$ element of the imaginary part of the RPA dielectric function of CdTe for $\vec{q}$ (in a.u.) along the (100) direction.

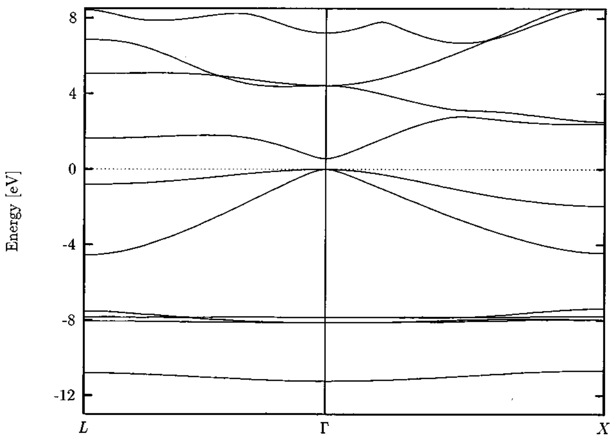

FIG. 3. The LDA band structure of CdTe. The flat, occupied bands at about -8 eV originate from the semicore Cd-4d states.

II-VI semiconductors with a II B element as a cation (Zn, Cd, or Hg), is the presence of a flat, occupied band due to localized cation, semicore d states,[6] which in the LDA calculations are placed about 8–10 eV below the Fermi level. Comparison with Fig. 2 suggests that a small peak in Im(ϵ) for $q=0$ at ~ 10 eV is caused by transitions from occupied Cd-4d bands into lowest and rather flat bands around the X point in the Brillouin zone. The important interband peak at 12–13 eV then originates from transitions between the occupied Cd-4d bands and the flat, unoccupied bands along Γ-L line. The upper panel of Fig. 4 proves this conjecture: it displays Im(ϵ) for $q=0$ calculated with and without transitions from Cd-4d states. The inset blows up the crucial energy region and gives additionally Re(ϵ). In passing, we want to mention that almost an identical plot, as represented by the dashed line, is obtained when Cd-4d electrons are treated as core electrons from the outset and a $5s$ and $5p$ pseudopotential at the cadmium atom is constructed. The lower panel of Fig. 4 shows the same for $q=0.4$ a.u. Its message is important for understanding the origin of the negative dispersion: although transitions from occupied Cd-4d states contribute to the strength of $\mathrm{Im}(\epsilon(q,\omega))$ for $\omega > 8$ eV and have a big influence on the shape of the loss function, their contribution is rather $\vec{q}$ independent. The negative dispersion is caused by other transitions, whose strength grows with growing $\vec{q}$ vector. A detailed inspection shows that these transitions are due to electron-hole transitions originating from the upper occupied valence bands. Therefore, the case of II-VI compounds resembles the case of the heavy-alkali metal Cs, where the growing strength of interband transitions into the unoccupied states was responsible for the negative plasmon dispersion with the growing $\vec{q}$ vector.[4]

We stress the role of the occupied Cd-4d states. For small $\vec{q}$ vectors their contribution to the strength of Im(ϵ) in the energy region of main loss peaks is almost as big as the contribution of the ‘‘tail’’ of the absorption peak obtained without transitions from Cd-4d states (see Fig. 4). Therefore, their effect on the shape of the loss function is very large. Without account of Cd-4d states, the loss spectrum is more peaked and plasmonlike. For larger $\vec{q}$ vectors, when the contribution due to other transitions is already substantial, the effect of Cd-4d states is smaller. This is, however, only half of the story of the role of Cd-4d states. It is well known that the LDA approximation underestimates the binding energy of these states and places them about 2 eV too high. This is a common feature of II-VI compounds[6] and other materials containing occupied localized electrons. Shifting down these states is a many-body self-energy effect beyond LDA.[7] An account of this effect at the first-principles level in a response calculation is at present an extremely difficult task. Therefore, we introduce empirically an additional attractive part in the Cd pseudopotential, which forces Cd-4d states to be close to their experimental position in the self-consistent bulk calculation. Since we work with *ab initio* nonlocal pseudopotentials,[12] it is possible to change the original pseudopotential only in its d component. In this way we include empirically the self-energy effects on the localized Cd-4d states.

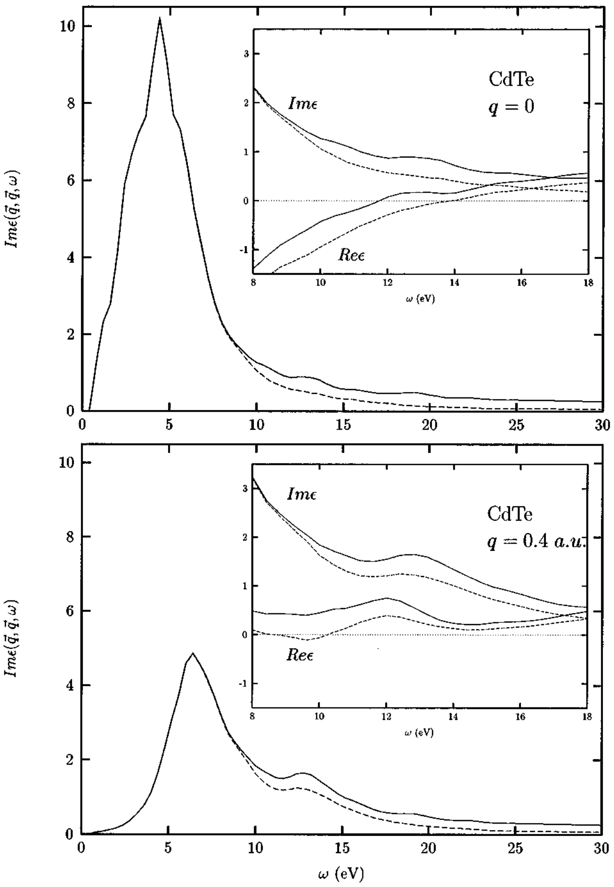

FIG. 4. The $\vec{G}=\vec{G}'=0$ element of the imaginary part of the RPA dielectric function of CdTe for $q=0$ (upper panel) and $q=0.4$ a.u. (lower panel) in the (100) direction. Solid line: full calculation, dashed line: transitions from the occupied Cd-4d states are supressed. The insets show the enlarged, important for the loss properties, energy part of the spectrum, with additionally real parts of ϵ included.

The loss function for CdTe calculated with these empirically renormalized Cd-4d states is shown in Fig. 5(a). The large effect of shifting down the Cd-4d states is clearly seen: although the position of most loss peaks remains essentially unchanged, the overall shape and relative height of them is significantly modified. For small $\vec{q}$ vectors the second, pre-

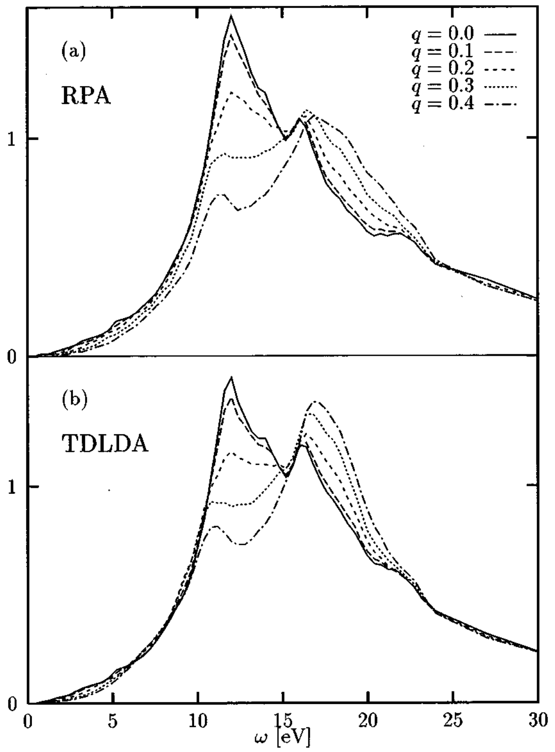

FIG. 5. The dispersion of the loss function of CdTe calculated within the RPA (a) and TDLDA (b) approximations for q (in a.u.) along the (100) direction. The ~2 eV self-energy shift down of Cd-4d states included in the way described in the text.

viously dominant peak, is largely supressed and the first, at 12 eV, strongly dominates the spectrum now. The negative dispersion of this peak is still present.

Inclusion of many-body exchange-correlation effects in screening, i.e., vertex corrections beyond the RPA, is another difficulty of the calculation of response functions even for the simplest systems. It can be concluded from calculations with an approximate inclusion of these effects, as well as from comparison with experiment, that in simple metals, exchange-correlation effects have a significant role in shifting the plasmon peaks for larger wave vectors to lower energies.[14] In the case of semiconductors and insulators, the matrix form of response functions Fourier transformed into reciprocal space, mixes small and large ($\vec{q}$ and $\vec{q}+\vec{G}$) wave vectors, thus enhancing the importance of exchange and correlation even for small q's. In a physical picture the short-wavelength density fluctuations (represented by large wave vectors) probe stronger the short-range exchange-correlation effects (described by the $f_{\rm xc}$ factor), than the long-wavelength fluctuations, determined mainly by the long-range RPA-type response.[10] A rough, yet computationally feasible way of including exchange-correlation effects in screening is within the *adiabatic* time-dependent local-density approximation (TDLDA).[8,9] This approximation for $f_{\rm xc}$ is real[15] and ω independent and known to show for larger wave vectors an incorrect q dependence.[16] Within TDLDA,

$$f_{\rm xc}(\vec{r},\vec{r}\,')=\frac{\delta V_{\rm xc}^{\rm LDA}(\vec{r})}{\delta n(\vec{r}\,')}, \qquad (4)$$

where $V_{\rm xc}^{\rm LDA}$ is the Kohn-Sham-LDA exchange-correlation potential. In Fig. 5(b), the dispersion of the loss function is shown with both effects included: the self-energy shift of Cd-4d states, and the exchange-correlation $f_{\rm xc}$ factor within the TDLDA approach. While for $q=0$ the TDLDA vertex increases the intensity of the peak at 16 eV, the main effect of this approximation is seen at larger q's. There, the energy of the negatively dispersing peak is slightly lowered, making the dispersion even more negative, while the intensity of upper peak is strongly enhanced.

Finally, let us mention that the crystal local-field effects, which show up as the effects of the matrix form in $\vec{G}$, $\vec{G}\,'$ of the response functions, are also rather strong in partly ionic II-VI compounds. As a consequence, the spectrum calculated in the diagonal approximation, i.e., with $\vec{G}=\vec{G}\,'=0$, is qualitatively different.[10]

Summarizing, we have studied the dynamical response of some II-VI compounds at the *ab initio* level. These materials show various unusual features in their electronic excitations and related loss functions: the main loss peak in these semiconductors has a negative dispersion, which was shown to originate from the interaction of electron-hole excitations with the plasmon collective excitation. The dynamical response depends strongly on various ingredients, such as the inclusion of the occupied semicore cation d states and their correct binding energy (a many-body, self-energy effect), the matrix form of the response functions and the effects of exchange and correlation via the vertex correction $f_{\rm xc}$. Our calculations are predictions: to the best our knowledge there are no measurements of the loss dispersion in these materials. The electron-energy loss experiment of Ref. 17 was done with rather low primary-electron energies and is not directly comparable with our calculations. The dispersion of loss features was not studied in this experiment. Nevertheless, in the case of CdTe, positions of measured peaks agree well with our calculations.

This work was supported by the Deutsche Forschungsgemeinschaft via the SFB 410 Project.

---

[1] G. D. Mahan, *Many-Particle Physics*, 2nd ed. (Plenum, New York, 1990).

[2] W. Schülke, H. Schulte-Schrepping, and J. R. Schmitz, Phys. Rev. B **47**, 12 426 (1994); N. E. Maddocks, R. W. Godby, and R. J. Needs, *ibid.* **49**, 8502 (1994); Europhys. Lett. **27**, 681 (1994); A. Fleszar, A. A. Quong, and A. G. Eguiluz, Phys. Rev. Lett. **74**, 590 (1995).

[3] A. vom Felde, J. Sprösser-Prou, and J. Fink, Phys. Rev. **40**, 10 181 (1989).

[4] F. Aryasetiawan and K. Karlsson, Phys. Rev. Lett. **73**, 1679 (1994); A. G. Eguiluz, A. Fleszar, and J. Gaspar, Nucl. Instrum. Methods Phys. Res. B **96**, 550 (1995); A. Fleszar, R. Stumpf, and A. G. Eguliuz, Phys. Rev. B **55**, 2068 (1997).

[5] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1965); W.

Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[6] S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988).

[7] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **75**, 3489 (1995); F. Aryasetiawan and O. Gunnarsson, Phys. Rev. B **54**, 17 564 (1996); A. Fleszar and W. Hanke (unpublished).

[8] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980); M. J. Stott and E. Zaremba, *ibid.* **21**, 12 (1980).

[9] E. K. U. Gross and W. Kohn, in *Density Functional Theory of Many-Fermion Systems*, edited by S. B. Trickey [Adv. Quantum Chem. **21**, 255 (1990)].

[10] W. Hanke and L. J. Sham, Phys. Rev. Lett. **43**, 387 (1979); Phys. Rev. B **12**, 4501 (1975); **21**, 4656 (1980).

[11] We have used the parametrization by P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981); of the results of D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[12] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[13] When transitions from occupied Cd-4d states are supressed, Im(ϵ) has a sharp peak at 13.2 eV. In the same time, the value of the *free electron* plasma frequency for $r_S = 2.4$, which corresponds to the average-electron density of CdTe, not counting Cd-4d electrons, is 12.7 eV.

[14] A. A. Quong and A. G. Eguiluz, Phys. Rev. Lett. **70**, 3955 (1993).

[15] It is *real* in the case of a homogeneous system. When applied to an inhomogeneous system, it results in the *hermiticity* of the $f_{\mathrm{xc}}(\vec{r},\vec{r}\,')$ operator.

[16] S. Moroni, D. M. Ceperley, and G. Senatore, Phys. Rev. Lett. **75**, 689 (1995).

[17] R. L. Hengehold and F. L. Pedrotti, Phys. Rev. B **6**, 2262 (1972).