TDDFT calculations for excitation spectra of $In_xGa_{1-x}As$ alloys

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(Dated: October 10, 2014)

We adopted the TDDFT theory and the cluster averaging method to compute the spectra of $In_xGa_{1-x}As$ with arbitrary concentration $x$. We find great agreement between theoretical and experimental data. The success of this method is mainly because that we approximate the transition matrix elements by the LDA p-matrix elements via meta-generalized gradient approximation (mGGA) which includes the singularity of the type $f_{XC,00}(q) \sim 1/q^2$ as $q \to 0$. Thus, Our studies provide some insight into the theoretical calculation of optical spectra of semiconductor alloys.

I. INTRODUCTION

The $In_xGa_{1-x}As$ alloys are very useful in the future because they can potentially outperform GaAs in electron transport properties and their room temperature band gaps are particularly well suited for applications in infrared emitting diodes and detectors\[1\]. Thus, it is highly desirable to have a better understanding of the electronic properties of these alloys. Kim and coworkers\[2\] reported the dielectric functions of selected compositions of different concentration $x$, including the endpoints values $x = 0$ and $x = 1$, which can be used as the database to analyze those with arbitrary concentration $x$. On the other hand, people can use many theoretical methods, like Bethe-Salpeter equation (BSE)\[3–7\] and time-dependent local density approximation (TDLDA)\[8, 9\], to calculate optical spectra for semiconductors and achieved good agreement with the experiment. These approaches focus on the response of the interacting system to a weak external perturbation and treat the exchange-correlation potential $V_{xc}$ by local density approximation (LDA)\[10\]. The difficulty, which has been known since the early 1980s, is that the basic local-density approximation and its semilocal extensions severely underestimate the band gap. A scissor operator $(\Delta E)P_{ck}$ must be used to correct the band gap for its application in solids. Here the energy shift $(\Delta E)$ is some constant which can be obtained either semiempirically\[11\] or by GW computation\[12–14\], and $P_{ck}$ is the projection operator applied on conduction bands only. Unfortunately, it’s impossible to use the scissor operator in alloy since it is a composition of two or more semiconductors and one can’t determine which band gap should be corrected. It prevents those theoretical methods to be applied to alloys.

The recent emerged meta-generalized gradient approximation (mGGA)\[15–17\] can fix the notorious underestimated band gaps caused by LDA\[15, 16\]. It expands the exchange-correlation potential in terms of not only the density, but also the gradient of the density $\nabla n_\sigma (r)$, the kinetic energy density $\tau (r)$, and(or) $\nabla^2 n_\sigma (r)$. Tran and Blaha’s(TB09) mGGA\[16\] shows great improvement in band gaps which can be in perfect agreement with experimental results. The mGGA can be used to generate Kohn-Sham(KS) wave functions and eigenenergies with good band gaps for GaAs, InAs and their alloys. The idea of using time-dependent density functional theory (TDDFT)\[20, 21\] with adiabatic mGGA to compute optical spectrum was adopted by Nazarov etc.\[22\]. They have implemented this approach into the full potential linearized augmented plane-wave (FPLAPW)\[24\] scheme to calculate optical spectrum for bulk Si and Ge with good success. However, FPLAPW needs a big number of plane waves as the basis which makes it not easy to be applicable to systems with large number of atoms. In this paper we will implement this approach into the full potential linearized augmented-slater-type-orbits (LASTO)\[25–28\] scheme with adiabatic mGGA to compute optical spectra for alloys. LASTO uses less number of basis than FPLAPW, which we believe makes it more competitive to be applied to big systems than the latter.

This paper is organized as follows. In Sec. II we briefly review the TDDFT concepts and formulas on which our calculation is based. In Sec. III we describe how to model the basic alloy structures needed in our calculation. Then Sec. IV apply the TDDFT approach to compute the optical absorption spectra for the family of ternary alloy $In_xGa_{1-x}As$. The results are compared to and gotten good agreement with experimental data. Finally, a short summary and outlook is presented to conclude the paper in Sec. V.

II. THEORETICAL METHODS

Let’s assume a weak perturbation to the alloy, then study the response of it to the perturbation. Theoretically, the excitonic information is contained in the com-
plex dielectric function $\varepsilon_M(q, \omega)$ via the response function $\chi$ given by

$$\frac{1}{\varepsilon_M(q, \omega)} = 1 + \frac{4\pi e^2}{q^2} \chi_{00}(q, \omega).$$

(1)

Here the response function $\chi$ can be built from the frequency-dependent, dynamical exchange-correlation (XC) kernel $f_{XC}(r, r', \omega)$ and the noninteracting KS response function $\chi_{KS}(r, r', \omega)$ by the equation

$$\chi^{-1}(r, r', \omega) = \chi^{-1}_{KS}(r, r', \omega) - f_{XC}(r, r', \omega) \frac{e^2}{|r - r'|},$$

(2)

where $f_{XC}(r, r', \omega)$ is defined as

$$f_{XC}(r, r', \omega) = \frac{\delta V_{XC}[n(r, \omega)]}{\delta n(r', \omega)},$$

(3)

where $f_{\nu}$ is the occupancy number for the Kohn-Sham state $|\Psi_{\nu, \sigma, k}(r)\rangle$ with quantum number $\nu$ and spin $\sigma$ at wave vector $k$ (limited in Brillouin zone). Note that the KS response function adapted in Eq. (3) is the static one, i.e., it doesn’t depend on time or frequency. One has to pay particular attention to the calculation of the matrix elements $\langle \Psi_{\nu, \sigma, k}(r)|e^{-i(G+q)\cdot r}|\Psi_{\nu', \sigma, k}(r)\rangle$ under mGGA. If the reciprocal vector $G$ is nonzero, it can be evaluated directly. If $G = 0$,

$$\langle \nu k | e^{-i q \cdot r} | \nu' k \rangle = \frac{1}{E_{\nu', k} - E_{\nu, k}} \langle \nu k | q \cdot v | \nu' k \rangle^{QP},$$

(6)

according to $k \cdot p$ perturbation theory. The velocity operator is given as $v = i[H, r]$. Under mGGA, the potential is nonlocal, thus $v = p + i[V(r), r]$, so one can’t use the momentum operator to replace the velocity operator. Since $[V(r), r]$ is hard to evaluate, we approximate the transition matrix elements on the right hand side of Eq. (6) by

$$\langle \nu k | v | \nu' k \rangle^{QP} = \frac{E_{\nu' k}^{QP} - E_{\nu k}^{QP}}{E_{\nu' k}^{LDA} - E_{\nu k}^{LDA}} \langle \nu k | v | \nu' k \rangle^{LDA}(\beta)$$

as was discussed by Rohlffing and Louie \[22\]. One can approximate the transition matrix elements $\langle \nu k | v | \nu' k \rangle^{LDA}(\beta)$ by the LDA p-matrix elements directly.

III. STRUCTURAL THEORIES OF ALLOYS

To calculate the dielectric functions for a ternary alloy $A_xB_{1-x}C$ with concentration $x$ of the constituent elements, we adopt the cluster-averaging method to simulate alloy systems. Firstly, five basic structures, $AC$, $BC$, $A_3B_4C_4$, $A_2B_3C_4$ and the 50%-50% alloy, have to be modeled and calculated at the corresponding lattice constant which obeys Vegard’s law \[30\] given by

$$a_{A_1-xB_xC} = xa_{AB} + (1-x)a_{AC}.\quad (8)$$

Their contributions are incorporated into the alloy of interest with occurrence probabilities $P^{(n)}(x)$

$$\varepsilon_M(q, \omega, a_x) = \sum_n P^{(n)}(x_n) \cdot \varepsilon_M(A_nB_{4-n}C_4, a_{x_n}),$$

(9)

where $a_x \equiv a_{A_1-xB_xC}$. We assume these probabilities are random and can be calculated by the equation

$$P^{(n)}(x) = \left(\frac{4}{n}\right) x^n(1-x)^{4-n}.\quad (10)$$

The binary end points compounds $AC$ and $BC$ are modeled by zinc blende structure withTd symmetry. The remaining thing is to model a 50%-50% alloy and two minority clusters $A_3B_4C_4$ and $A_2B_3C_4$. It is not trivial because atoms are randomly distributed over the sample in alloys and we want to take advantage of a periodic unit cell. We follow the procedure described in Ref. \[31\]. The 50%-50% alloy is modeled by the primitive tetragonal structure with space group No. 115 in the International Tables for Crystallography or point group $D_{2d}$. It
contains 4 atoms per unit cell with the primitive vectors

\[ a_1 = \left( \frac{1}{2}, -\frac{1}{2}, 0 \right) a_{0.5}, \]
\[ a_2 = \left( \frac{1}{2}, \frac{1}{2}, 0 \right) a_{0.5}, \]
\[ a_3 = (0, 0, 1) a_{0.5}, \]

where the \( a_{0.5} \) is the face-centered cubic lattice constant. Two minority clusters \( A_3BC_4 \) and \( AB_3C_4 \) require a larger unit cell to model them, and we use the primitive cubic structure with space group No. 215 or point group \( T_d \), which contains 8 atoms unit cell with the primitive vectors

\[ a_1 = (1, 0, 0) a \]
\[ a_2 = (0, 1, 0) a \]
\[ a_3 = (0, 0, 1) a. \]

In principle, we can use three distinct unit cells for five clusters, the typical zincblende unit cell for \( AC \) and \( BC \), the primitive tetragonal structure for 50%-50% alloy, and the primitive cubic structure for 25%-75% and 75%-25% alloys. In order to cancel systematic errors, we use the largest unit cell among them, the one specified by Eq. (12), for the latter three alloys. Their constituent atoms are allowed to relax until they reach equilibrium positions. In general, all atoms can move independently, but we restrict their movements in a way preserving the symmetry of the atoms in their unrelaxed (ideal) positions in the crystal. Note that we don’t use the largest unit cell for \( AC \) and \( BC \) since we found the results of both the supercell and the bulk are the same.

### IV. RESULTS AND DISCUSSION

The self-consistent KS band structures of \( GaAs \), \( InGaAs_4 \) \( InGaAs_2 \) \( InAsGaAs_4 \) and \( InAs \) were computed with TB09 \[16\] mGGA and LASTO basis scheme. For the 50%-50% alloy \( InGaAs_2 \), for 25%-75% alloy \( InGaAs_4 \) and 75%-25% alloy \( InAsGaAs_4 \), their lattice constants are 11.06868 Bohr, 10.87443 Bohr, 11.25710 Bohr. The unit cell for all three alloys are supercell with basis vectors given by Eq. (12). Since LASTO uses point group to do the calculation, we used D2d symmetry for the 50%-50% alloy \( InGaAs_2 \), and Td symmetry for the primitive cubic structure for 25%-75% alloy \( InGaAs_4 \) and 75%-25% alloy \( InAsGaAs_4 \). The coordinates of relaxed atoms of the alloys are listed in Table I. Based on the band structures, we calculated optical spectra for five basic structures, using TDDFT with the transition matrix elements approximated by the LDA p-matrix elements, as described by Eq. (7), via mGGA. We used a 8x8x8 k-mesh for supercells and 10x10x10 k-mesh for bulk structures, generated by Monkhorst-Pack method with shift (0.083333, 0.25, 0.416667)\( \frac{2\pi}{a} \), to do the Brillouin zone integration. The cutoffs of the reciprocal vectors were set to 2.3 for bulk structures and 2.0 for supercells. The average value of the derivative of the XC energy with respect to the kinetic energy density in Eq. (6) were computed by Voorhis and Scuseria’s XC functional [17]. Their spectra are presented in Fig 2.

Then we adopted the cluster averaging method to calculate the optical spectra of alloy \( In_xGa_{1-x}As \) with arbitrary concentration \( x \) and fit them to experimental data. The real and imaginary parts of spectra are presented in Fig 3. It is obvious that TDDFT with the transition matrix elements approximated by the LDA p-matrix elements via mGGA, as described by Eq. (7), greatly improves the agreement between the theoretical and experimental data.

Since LASTO uses less number of basis functions than other schemes, this makes TDDFT+GGA within

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**TABLE I:** The Cartesian coordinates of atoms of relaxed alloys \( InGaAs_2 \), \( InGaAs_4 \) and \( InAsGaAs_4 \).

| \( InGaAs_2 \) | \( InGaAs_4 \) | \( InAsGaAs_4 \) |
|----------------|----------------|-----------------|
| \( In_1(0, 0, 0) \) | \( In_1(0, 0, 0) \) | \( Ga_1(0, 0, 0) \) |
| \( In_2(0.5, 0.5, 0) \) | \( Ga_2(0.5, 0.5, 0) \) | \( In_3(0.5, 0.5, 0) \) |
| \( Ga_4(0.5, 0.5, 0) \) | \( Ga_3(0.5, 0.5, 0) \) | \( In_3(0.5, 0.5, 0) \) |
| \( As_2(0.7503, 0.7503, 0.2705) \) | \( As_2(0.2596, 0.2596, 0.2705) \) | \( As_2(0.2395, 0.2395, 0.2395) \) |
| \( As_3(0.2497, 0.2497, 0.7295) \) | \( As_2(0.7404, 0.7404, 0.2706) \) | \( As_3(0.7605, 0.7605, 0.2395) \) |
| \( As_4(0.2497, 0.7503, 0.7295) \) | \( As_2(0.7404, 0.2596, 0.7404) \) | \( As_4(0.7605, 0.2395, 0.7605) \) |

**FIG. 1:** Optical spectra of five basic structures.
FIG. 2: Optical spectra of alloys In$_x$Ga$_{1-x}$As. Colored and solid lines are results obtained with cluster averaging method, except for $x=0$ and $x=1$ whose results are computed with mGGA band structures including the many-body interactions through $f_{XC}$ given by Eq. (3). Colored and dashed lines are experimental data from Ref.[2].

LASTO is fast and efficient enough to handle large supercells, up to 100 atoms. Thus it can be applied to novel material and those with big number of atoms, like buckyball, quantum dots and solar cell. On the other hand, LASTO basis allows us to extract interaction parameters within tight-binding model, which can be combined with TDDFT to treat realistic nanoparticles semi-empirically.

V. CONCLUSION

We used the TDDFT theory with the transition matrix elements approximated by the LDA p-matrix elements via mGGA and the cluster averaging method to compute the spectra of In$_x$Ga$_{1-x}$As with arbitrary concentration $x$ and compared them to experimental results. It turns out the great success of this method. This method is simple and time saving. The main reason is that mGGA provides approximately correct band structures for alloys so that the expensive GW correction or inapplicable rigid scissor operator is no longer needed in our calculation. We believe this method can be applied in more materials, especially some with special structures, like superlattice, in the future.

ACKNOWLEDGMENTS

We wish to acknowledge the support of Research Center for Applied Sciences, Academia Sinica, Taiwan, ROC in using supercomputer.

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