LOCAL BASIS GW CALCULATIONS AND THE DIELECTRIC RESPONSE OF Si AND C CLUSTERS

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ABSTRACT

We describe our progress in developing an ab initio computational scheme for the calculation of the dielectric response function of solids, with special emphasis here on Si and C clusters. All calculations are carried out employing a basis of localized atomic-like orbitals and include the evaluation of quasiparticle corrections. The self-energy operator is evaluated in the GW approximation, with a full frequency dependence for the dielectric matrix. The approach is convenient and computationally optimal for the calculation of optical properties of complex systems lacking full periodicity, such as surfaces and clusters. We present here the dielectric response functions of clusters with structures found after full equilibration via molecular dynamical simulations, and discuss the sensitivity of the optical properties to quasiparticle corrections.

INTRODUCTION

The optical properties of materials define an area of continuing interest. It is then important to be able to carry out reliable and efficient calculations of these properties from first principles. The successes in the calculation of structural and overall electronic properties of solids starting using the density functional theory (DFT) and the local density approximation (LDA) are well-known. However, the calculation of excitations for optical and conductivity response are still an area of current activity, mostly because of the high computational cost for suitable comparison with experiments.

We report here our advances in the implementation of a local-basis calculation of the Hedin's GW approach to this general problem. In particular, we discuss our results for silicon and carbon clusters, to illustrate the role of symmetries and different bonding environments. Notice that the sp² bonding present in carbon clusters yields more extended states than the sp³ predominant in the silicon structures, and would test this implementation on different aspects. Our calculations provide a successful description of the low-energy excitations at moderate computational expense. The features seen in photoabsorption experiments of C clusters agree qualitatively with our calculations, despite our neglecting excitonic effects.

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METHOD

Studying optical properties, we concentrate on the macroscopic dielectric function [1],

\[ \varepsilon^M(\omega) = \lim_{q \to 0} \frac{1}{[\varepsilon^{-1}]_{q+G, q, \omega}} \]

Here \( \varepsilon(q, \omega) \) is the symmetrized dielectric matrix with elements defined within the random phase approximation as

\[
\varepsilon_{GG'}(q, \omega) = \delta_{GG'} + \frac{8\pi e^2}{\Omega} \sum_{\text{occ}} \sum_{\text{unocc}} \sum_{m} \sum_{k} M_{\text{G}n}^{\text{Gm}}(k, q) [M_{\text{G}m}^{\text{Gn}}(k, q)]^* \\
\times \left\{ \frac{1}{\varepsilon_{n,k,q} - \varepsilon_{m,k} + \omega + i\eta} + \frac{1}{\varepsilon_{m,k,q} - \varepsilon_{n,k} - \omega + i\eta} \right\},
\]

where \( \varepsilon_{n,k} \) is the quasiparticle energy, and \( M_{\text{G}m}^{\text{Gn}}(k, q) \equiv \langle n, k - q | e^{-ik+G} | m, k \rangle \) is the transition matrix element between the wave functions \( |n, k - q\rangle \) and \( |m, k\rangle \), and the \( n \) (\( m \)) sums are over unoccupied (occupied) states.

As mentioned above, a very practical method to solve the quasiparticle problems in the GW approximation. As others in the literature, we start from the DFT-LDA Green's function and incorporate the screened interaction at the same level [2]. The quasiparticle energy is obtained in the GW approach considering the real part of the self-energy correction, \( \Sigma(\omega) \), with respect to the DFT-LDA exchange-correlation potential \( V^{\text{xc}} \),

\[
\varepsilon_{n,k} = \varepsilon_{n,k}^{\text{LDA}} + Z_{n,k} \langle n, k | (\text{Re} \Sigma(\omega = \varepsilon_{n,k}^{\text{LDA}}) - V^{\text{xc}}) | n, k \rangle,
\]

\[
Z_{n,k} = \left[ 1 - \frac{\partial \text{Re} \Sigma(\omega)}{\partial \omega} \bigg|_{\omega = \varepsilon_{n,k}^{\text{LDA}}} \right]^{-1}.
\]

In our GW calculation, we adopt a set of polarized pseudo-atomic orbitals (PAO) as the basis functions. The single-particle electronic eigenstates can be written as a linear combination of such PAO's positioned at the atomic coordinates \( R_i \),

\[
|n, k\rangle = \frac{1}{\sqrt{N}} \sum_{L} \sum_{\mu l} \phi_{n,k}^{\text{PAO}}(x - R_i - L).
\]

The eigenvalues \( \varepsilon_{n,k}^{\text{LDA}} \) and the corresponding eigenstates \( |n, k\rangle \) in Eq. (3) are obtained using the local-orbital density-functional method developed by Sankey and co-workers [3] and extended to \( d \)-orbitals by Yang [5]. The method has been shown to be reliable, and with execution times much shorter than other \textit{ab initio} methods. The use of a localized basis set is extremely convenient to study the structural equilibration and corresponding electronic structure of various solids, including clusters or disordered systems. Specially, it is found that nine orbitals per atom \((sp^3d^2)\) are sufficient to perform calculations for most semiconductors [4], providing band structures similar to other methods specifically designed for that task.

The matrix element of the real part of the self-energy operator required in the quasiparticle energy calculation, Eq. (3), is given by

\[
\langle n, k | \text{Re} \Sigma(\omega) | n, k \rangle = \frac{8\pi e^2}{\Omega} \sum_{GG'} \sum_{q} \sum_{m} M_{Gn}^{Gm}(k, q) [M_{Gm}^{Gn}(k, q)]^* \]
\begin{align}
\times \operatorname{Re} \tilde{\bar{\epsilon}}_{G\nu}(\mathbf{q}, \omega - \varepsilon_{m,k+q}) + \sum_{G,G', a,m,z} \sum_{q} \sum_{m} M_{G\nu}^{zm}(k, q) \left[ M_{G\nu}^{zm}(k, q) \right]^* |q + G| |q + G'|
\times P \int_0^{\infty} \frac{d\omega'}{\omega'} \operatorname{Im} \tilde{\bar{\epsilon}}_{G\nu}(\mathbf{q}, \omega') \text{sgn}(\omega') \right)
\end{align}

The symmetrized inverse dielectric matrix-elements $\tilde{\bar{\epsilon}}_{G\nu}(\mathbf{q}, \omega)$ are obtained by direct inversion of the matrix $\tilde{\bar{\epsilon}}(\mathbf{q}, \omega)$ for the needed values of $\mathbf{q}$ and $\omega$. The $\tilde{\bar{\epsilon}}_{G\nu}(\mathbf{q}, \omega)$ matrix-elements are rescaled to enforce the $F$-sum rule [6]. The $\omega'$-integral in Eq. (5) is performed by considering the frequency dependence of $\tilde{\bar{\epsilon}}_{G\nu}(\mathbf{q}, \omega')$. This is particularly important for systems where the plasmon modes merge with the single-particle excitations at finite $\mathbf{q}$, for which the plasmon-pole model fails. The $V_{xx}$ potentials are of the Ceperley-Alder form, as parameterized by Perdew and Zunger [7]. The renormalization factor $Z_{m,k}$ is obtained numerically by evaluating the energy-dependence of the self-energy around each $\epsilon_{m,k}^{0,0}$. The method has been tested on bulk-Si, yielding results which compare well to other GW calculations [8]. In the quasiparticle calculations of $\text{Si}_{40}$ and $\text{C}_{40}$ clusters here, we use supercells of $20 \times 20 \times 20$ Å$^3$, large enough to ensure that each cluster is isolated. The transition matrix-elements $M_{G\nu}^{zm}(k, q)$ were calculated using a Fourier representation with over 850 G-vectors, to achieve a good description within a convergence of $10^{-2}$. The imaginary part of the self-energy is also analyzed to evaluate the lifetime of the quasiparticle. We find that it has a small magnitude for all states, and smaller than $10^{-2}$ eV at most of the energy levels, showing the good stability of the quasiparticle excitations.

**C$_{40}$ CLUSTERS**

As is well known, the $\text{C}_{40}$ cluster consists of twenty hexagons and twelve pentagons, involving an $sp^3$ and $sp^2$ hybridization, respectively. The isolated $\text{C}_{40}$ cluster has icosahedral symmetry ($I_a$) and its energy levels have up to five-fold degeneracies. We calculate the HOMO-LUMO gap ($e_6 \rightarrow e_1$) as 1.77/2.05 eV before/after GW corrections. Correspondingly, the lowest six optically allowed excitation energies are calculated after the GW corrections at 3.18 ($e_6 \rightarrow e_{18}$), 3.32 ($e_3 \rightarrow e_{18}$), 4.27 ($e_6 \rightarrow e_{24}$), 5.29 ($e_5 \rightarrow e_{24}$), 5.43 ($e_5 \rightarrow e_{24}$), and 5.91 eV ($e_6 \rightarrow g_6$), respectively. The experimental photoabsorption spectrum of the $\text{C}_{40}$ clusters in a hexane solution [9] exhibits a relatively weak onset at $\approx 2.2$ eV, a shoulder feature at 3.1 eV and sharper UV peaks at 3.8, 4.8, and 5.8 eV. Our results are consistent with the experimental measurements.

The dielectric response functions calculated before (dotted curve) and after (solid curve) GW corrections are presented in Fig. 1. The quasiparticle GW corrections do not result in significant changes of the shape of the response function, but open the optical gap by $\approx 0.3$ eV. Notice that the first four peaks in $L_{xx}$ are shifted to higher frequency with only slight changes in their relative weights. Those peaks are clearly related to the visible and UV features observed in experiments [9]. We should state, however, that the relative amplitudes of the peaks differ from those in experiments somewhat, perhaps due to excitonic effects ignored in this calculation (see below).

**Si$_{40}$ CLUSTERS**

The equilibrium structure of Si$_{40}$ clusters does not result in the high symmetry of the $\text{C}_{40}$ clusters, but rather exhibits a more compact geometry which favors four-fold bonding envi-
Figure 1: Imaginary part (in arbitrary units) of the macroscopic dielectric function $\varepsilon^i(\omega)$ of $C_{60}$ cluster. The solid (dotted) curve indicates results after (before) GW corrections. Feature broadening in plot is 0.1 eV, comparable to experimental resolution.

correlations for nearly all atoms in the cluster (see Fig. 2). This behavior has been attributed to various reasons, although the larger core size in Si seems to suppress $sp^3$ bonding and result in the $sp^2$ bonds which determine the electronic properties. Due to the lower symmetry of the structure, the energy levels of the Si$_{60}$ cluster are nearly non-degenerate, and the HOMO $\rightarrow$ LUMO gap is much narrower than in the C$_{60}$ cluster (0.55/1.45 eV before/after the GW corrections).

The imaginary part of the dielectric response function of the Si$_{60}$ cluster in the energy region of interest is presented in Fig. 3, both before (dotted curve) and after the full GW correction (solid). The enhancement of the optical gap due to quasiparticle corrections is clearly seen in the figure. Moreover, the shape of the dielectric response function is enhanced slightly near the first absorption peak, producing an overall smoothing and oscillator strength redistribution. We should point out that these results are in qualitative agreement with recent photoluminescence measurements in Si clusters created by annealing of implanted samples. There, features at $\approx 1.5$ eV are seen and identified with the aggregation of nanoclusters and the associated quantum confinement effects on electrons, in addition to possible surface defects and reconstruction [11].

CONCLUSIONS

We have calculated the dielectric response functions of C$_{60}$ and Si$_{60}$ clusters using a GW approach in a local basis set of pseudatomic orbitals implemented recently [8]. The approach is aimed at the study of optical properties of semiconductors and insulators using a local basis set at a moderate computational cost. We find that the GW corrections significantly enhance the optical gap by 0.9 eV in Si$_{60}$ and 0.28 eV in C$_{60}$ from the DFT-LDA results. The dielectric response functions obtained after the GW corrections show good agreement with the corresponding absorption spectrum obtained in experiments [9, 11]. Notice, however, that excitonic effects related to the two-particle self-energy terms in the electron-hole inter-
Figure 2: The equilibrium structure of the $S_{50}$ cluster obtained using \textit{ab initio} molecular dynamical simulations (Ref. [10]).

Figure 3: Imaginary part (in arbitrary units) of the macroscopic dielectric function $\varepsilon^M(\omega)$ for $S_{50}$. The solid (dotted) curve indicates results after (before) GW corrections. Feature broadening in plot is 0.1 eV.
action are believed to be non-negligible in finite-size systems due to the weaker screening of the Coulomb interaction [12]. For Si nanocrystals, for example, the exciton effect reduces the band gap corrected by GW, and gives an optical gap which is in better agreement with experiments [12]. Incorporation of these effects for $C_{60}$ and $Si_{60}$ clusters within our local-basis formulation may indeed reduce the larger gaps we find here. The implementation of these and full self-consistency remain as future challenges, which we anticipate would be made computationally simpler in our local basis.

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References


