

Local-basis quasiparticle calculations and the dielectric response function of Si clusters

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We present an *ab initio* computational scheme for evaluating the dielectric response function of Si clusters. All calculations are carried out employing a basis of localized atomiclike orbitals and including 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 quasiparticle-level structure for Si₂₀ and Si₆₀ clusters and discuss the sensitivity of their optical properties to quasiparticle corrections. We find that the optical gap is larger than in bulk silicon, clearly the net result of size quantization over structural disorder.

Computer modeling of electronic and optical properties of materials is one of the most promising and rapidly developing areas of condensed matter theory. To a large degree, *structural* (and ground-state properties in general) are well described by density-functional theory in the local-density approximation (LDA). Other quantities of obvious importance, including electronic, transport, and optical response functions are only qualitatively described in the LDA and it is of special importance to devise new methods that provide *accurate estimates of excited states* and associated properties *at tolerable computational efficiency*. It is with a view to meeting *both* of these criteria that we introduce a *real-space* implementation of Hedin's "GW" approximation¹ and apply it to Si clusters. Our work provides both some insights into the electronic properties of these clusters, and suggests a path towards a full real space version of the GW approximation, which we expect to have utility in any system lacking full translational periodicity.

A systematic approach to calculate quasiparticle excitation energies is based on the solution of the following equation:

$$\begin{aligned} H_0(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}, \omega) + \int d^3r' \Sigma(\mathbf{r}, \mathbf{r}', \omega)\psi_{n\mathbf{k}}(\mathbf{r}', \omega) \\ = \varepsilon_{n\mathbf{k}}(\omega)\psi_{n\mathbf{k}}(\mathbf{r}, \omega), \end{aligned} \quad (1)$$

where H_0 is the Hartree Hamiltonian, and $\varepsilon_{n\mathbf{k}}(\omega)$ and $\psi_{n\mathbf{k}}(\mathbf{r}, \omega)$ are the quasiparticle energy and wave function, respectively. The nonlocal and energy-dependent self-energy operator $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$ contains formally all the effects of exchange and correlation. It is in general a complex quantity, where the imaginary part describes the damping of the quasiparticle. Calculations of $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$ are difficult even for the uniform electron gas, as there is no explicit solution for the vertex function, in general. The simplest working approximation was introduced by Hedin in 1965,¹ in which the vertex is approximated by the lowest-order function, so that the $\Sigma(\mathbf{r}, \mathbf{r}', \omega)$ is given by the product of the Green's function and the screened Coulomb interaction $W(\mathbf{r}, \mathbf{r}', \omega')$

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int d\omega' e^{-i\eta\omega'} G(\mathbf{r}, \mathbf{r}', \omega - \omega') W(\mathbf{r}, \mathbf{r}', \omega'), \quad (2)$$

with

$$G(\mathbf{r}, \mathbf{r}', \omega) = \sum_{n\mathbf{k}} \frac{\psi_{n\mathbf{k}}(\mathbf{r}, \omega)\psi_{n\mathbf{k}}^*(\mathbf{r}', \omega)}{\omega - \varepsilon_{n\mathbf{k}}(\omega) - i\eta \operatorname{sgn}[\mu - \varepsilon_{n\mathbf{k}}(\omega)]}, \quad (3)$$

$$W(\mathbf{r}, \mathbf{r}', \omega') = \int d^3r'' v(\mathbf{r} - \mathbf{r}'') \varepsilon^{-1}(\mathbf{r}'', \mathbf{r}', \omega'). \quad (4)$$

Here, μ , $v(\mathbf{r} - \mathbf{r}')$, and $\varepsilon^{-1}(\mathbf{r}, \mathbf{r}', \omega')$ are respectively the chemical potential, the bare Coulomb interaction, and the inverse dielectric function, and η is an infinitesimal convergence factor.

A number of successful computational efforts based on the GW framework have been presented over the last decade.² Most of the calculations start from the LDA band structure and employ a set of plane-wave (PW) basis functions. A plasmon-pole model has been used to simplify the frequency dependence of the screened Coulomb interaction, and to reduce computational costs. In this framework, it has been shown that the GW corrections bring the quasiparticle band-structure into good agreement with experiment for many semiconductors, metals, and insulators.^{2,3} In such calculations, a large number of PW's are typically needed, especially for more complex systems, such as surfaces and clusters, and in general, solids with large unit cells or systems with "hard" pseudopotentials. Recently, some efforts have been made to reduce the requirement of large basis function sets. Rohlfling *et al.*⁴ have implemented an efficient scheme for quasiparticle calculations employing localized Gaussian orbitals as a basis. The applications to bulk and surface systems showed a reduction on the computation time and produced the same accuracy as using a PW basis. For bulk Si, for example, the number of Gaussian orbitals needed to perform the GW calculation is 40-60 per unit cell, whereas 350 PW's are needed in the conventional approach.⁴

In this paper, we present a different GW approach using a localized-function basis set for the calculation of optical

properties. The local functions are a set of polarized atomic orbitals (PAO), which have been used successfully in the density-functional molecular dynamics developed by Sankey and co-workers,⁵ as well as in more recent work by Ordejón *et al.*⁶ These implementations have been shown to be reliable, and with execution times much shorter than other *ab initio* methods. The use of a localized basis set is extremely convenient to study the structural equilibration and corresponding electronic structure of systems lacking translation invariance. In particular, nine orbitals per atom (sp^3d^5) are found to be sufficient to perform calculations for most semiconductors,⁷ and provide band structures similar to other methods specifically designed for that task. Taking this into consideration, we have developed our GW quasiparticle and optical function calculation in the framework of this efficient local basis. An additional feature of our calculations here, and possible due to the efficiency of our approach, is that instead of using the simple plasmon pole model to approximate the calculation of the dielectric matrix elements, we take into account the full frequency dependence of the dielectric matrix. Our aim is to have a highly accurate formulation for the study of the optical properties of complex systems, such as surfaces and clusters. The first application of our approach is to the study of Si₂₀ and Si₆₀ clusters, as well as bulk silicon.

In general, Eq. (1) has to be solved self consistently with respect to the charge density $\rho(\mathbf{r})$ and the quasiparticle energies entering the expressions (2) and (3). In most GW calculations performed, however, the self-energy operator is obtained assuming the LDA Green's function, and incorporating the screened interaction in $W(\mathbf{r}, \mathbf{r}', \omega')$ at the same level.²⁻⁴ For convenience, we also make this approximation in our present work, although a fully self-consistent treatment is clearly possible (see discussion below). Furthermore, the quasiparticle energy is obtained considering the real part of the self-energy correction with respect to the LDA exchange-correlation potential V^{xc} ,

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

$$Z_{n\mathbf{k}} = \left[1 - \frac{\partial \text{Re} \Sigma(\omega)}{\partial \omega} \Big|_{\varepsilon_{n\mathbf{k}}^{LDA}} \right]^{-1}, \quad (5)$$

where the renormalization factor $Z_{n\mathbf{k}}$ arises from the energy dependence of the self-energy.

The diagonal matrix-element of the self-energy operator $\langle n\mathbf{k} | \Sigma(\omega) | n\mathbf{k} \rangle$ is conveniently implemented in a Fourier representation, since the screened interaction $W(\mathbf{r}, \mathbf{r}', \omega)$ can be written in terms of the *inverse* dielectric matrix-elements,

$$W(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\mathbf{G}, \mathbf{G}'} \sum_{\mathbf{q}}^{BZ} e^{i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} \times \frac{4\pi e^2}{V |\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'|} \tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega) e^{-i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}'}, \quad (6)$$

$$\tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) = \delta_{\mathbf{G}, \mathbf{G}'} + \frac{8\pi e^2}{V |\mathbf{q} + \mathbf{G}| |\mathbf{q} + \mathbf{G}'|} \times \sum_{c, v} \sum_{\mathbf{k}} M_{\mathbf{G}}^{vc}(\mathbf{k}, \mathbf{q}) [M_{\mathbf{G}'}^{vc}(\mathbf{k}, \mathbf{q})]^* \times \left\{ \frac{1}{\varepsilon_{c\mathbf{k}-\mathbf{q}} - \varepsilon_{v\mathbf{k}} + \omega + i\eta} + \frac{1}{\varepsilon_{c\mathbf{k}-\mathbf{q}} - \varepsilon_{v\mathbf{k}} - \omega + i\eta} \right\}. \quad (7)$$

Here, $v(c)$ denotes the valence/filled (conduction/empty) bands, V is the volume of the system, and the \mathbf{q} sum is over the first Brillouin zone.⁸ The symmetrized dielectric matrix-element $\tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega)$ is calculated within the random phase approximation, as vertex corrections are neglected in the GW approximation. The symmetrized inverse dielectric matrix-elements $\tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega)$ are obtained by direct inversion of the matrix $\tilde{\varepsilon}(\mathbf{q}, \omega)$ for the needed values of \mathbf{q} and ω . The $\tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega)$ matrix-elements are rescaled to enforce the f -sum rule.³

The matrix element of the real part of the self-energy operator required in the quasiparticle energy calculation [Eq. (5)] is given by

$$\langle n\mathbf{k} | \text{Re} \Sigma(\omega) | n\mathbf{k} \rangle = - \frac{8\pi e^2}{V} \left\{ \sum_{\mathbf{G}, \mathbf{G}'} \sum_{\mathbf{q}}^{BZ} \sum_m^{occ} \frac{M_{\mathbf{G}}^{mn}(\mathbf{k}, \mathbf{q})}{|\mathbf{q} + \mathbf{G}|} \frac{[M_{\mathbf{G}'}^{mn}(\mathbf{k}, \mathbf{q})]^*}{|\mathbf{q} + \mathbf{G}'|} \text{Re} \tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega - \varepsilon_{m\mathbf{k}-\mathbf{q}}) + \sum_{\mathbf{G}, \mathbf{G}'} \sum_{\mathbf{q}}^{BZ} \sum_m \frac{M_{\mathbf{G}}^{mn}(\mathbf{k}, \mathbf{q})}{|\mathbf{q} + \mathbf{G}|} \frac{[M_{\mathbf{G}'}^{mn}(\mathbf{k}, \mathbf{q})]^*}{|\mathbf{q} + \mathbf{G}'|} P \int_0^\infty \frac{d\omega'}{\pi} \frac{\text{Im} \tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega') \text{sgn}(\omega')}{\omega - \omega' - \varepsilon_{m\mathbf{k}-\mathbf{q}}} \right\}. \quad (8)$$

The ω' -integral in Eq. (8) is performed by considering the full frequency dependence of $\tilde{\varepsilon}_{\mathbf{G}, \mathbf{G}'}^{-1}(\mathbf{q}, \omega')$. 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 transition matrix-element $M_{\mathbf{G}}^{mn}(\mathbf{k}, \mathbf{q}) \equiv \langle m\mathbf{k} - \mathbf{q} | e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} | n\mathbf{k} \rangle$, which appears both in the dielectric matrix element [Eq. (7)] and in the self energy

[Eq. (8)], can be calculated either in a real space or in a reciprocal space representation. The former is found more suitable for a localized system, such as the clusters considered here. The V^{xc} potentials are of the Ceperley-Alder form, as parameterized by Perdew and Zunger.⁹ The renormalization factor $Z_{n\mathbf{k}}$ is obtained numerically by evaluating the energy-dependence of the self energy around each $\varepsilon_{n\mathbf{k}}^{LDA}$. A

TABLE I. Calculated band-structure energies of Si at high symmetry points (in eV). The lattice constant is the experimental value of 5.43 Å. A 125 k -point grid and ten special \mathbf{q} points were used in our GW calculation, with 80- \mathbf{G} vectors. The von der Linden-Horsch plasmon-pole model was used in all dielectric matrix calculations (Ref. 15). The LDA calculation of the third column and the GW calculation of the sixth column were performed by Rohlffing *et al.* (Ref. 4) and GW result of seventh column was by Hybertsen and Louie (Ref. 3). Number of orbitals per unit cell (with two atoms) is in parenthesis. The experimental values are from Ref. 13.

k -point	LDA (8 PAO) sp^3	LDA (18 PAO) sp^3d^5	LDA (60 GO) Ref. 4	GW (8 PAO) sp^3	GW (18 PAO) sp^3d^5	GW (60 GO) Ref. 4	GW (PW) Ref. 3	Expt. Ref. 13
Γ_{25v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Γ_{15c}	2.21	2.67	2.57	3.54	3.70	3.36	3.35	3.40
X_{4v}	-3.35	-2.63	-2.78	-3.72	-2.75	-2.93	-2.99	-2.9, -3.3
X_{1c}	2.90	0.48	0.65	4.24	1.28	1.43	1.44	1.25
L_{3v}	-1.54	-0.98	-1.17	-1.74	-1.22	-1.25	-1.27	-1.2, -1.5
L_{1c}	2.38	1.72	1.47	3.70	2.89	2.19	2.27	2.1, 2.4

detailed description of our computational scheme will be presented elsewhere.¹⁰

To analyze the optical properties, we concentrate on the macroscopic dielectric function,¹¹

$$\epsilon^M(\omega) = \lim_{\mathbf{q} \rightarrow 0} \frac{1}{\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)|_{\mathbf{G}=\mathbf{G}'=0}}. \quad (9)$$

The inverse dielectric matrix $\epsilon^{-1}(\mathbf{q}, \omega)$ has, in general, non-vanishing off-diagonal elements due to lattice periodicity, and the proximity of atoms around the central unit cell, both of which influence the optical spectra. Calculation of the macroscopic function via Eq. (9) allows one to study various optical properties, such as the absorption spectra, which is directly related to the imaginary part of dielectric function $\text{Im} \epsilon^M(\omega)$; the dielectric constant $\epsilon_0 = \text{Re} \epsilon^M(0)$; as well as the electronic contribution to the frequency-dependent conductivity $\sigma(\omega)$ under the relation of $\epsilon(\omega) = 1 + (4\pi i/\omega)\sigma(\omega)$.¹² The global local field (LF) effects in $\epsilon^M(\omega)$ are important in bulk/extended systems, but obviously disappear when the system becomes dilute, such as in the clusters considered here. Notice, however, that the ‘‘polarizability’’ of all the atoms *in the cluster* (i.e., the intra-cluster LF) is explicitly taken into account in our approach. On the other hand, intercluster LF effects would appear if one is, for example, describing a nanostructured solid, where clusters are assembled in close proximity, and embedded in some sort of matrix.¹¹

As an initial test of our method, we have calculated the band structure of bulk Si near both the valence- and conduction-band edges. Two different sets of basis orbitals are used, the minimal basis of sp^3 orbitals and the larger basis of sp^3d^5 orbitals per atom. The results at high-symmetry points are given on Table I. As can be seen there, the results at the LDA level for the band structure require d orbitals to be fully converged (see first two columns), and show the well-known indirect $\Gamma_{25v} \rightarrow X_{1c}$ (approximately) gap in silicon (if grossly underestimated by ≈ 0.8 eV for 18 PAO, as is typical in LDA calculations.^{2,3}) On the other hand, the GW corrections using either the minimal basis set

[GW(8 PAO)] or larger basis set [GW(18 PAO)] are comparable (although $\approx 20\%$ smaller for the larger PAO set), indicating good convergence in our GW correction with respect to the size of the basis functions. Notice however, that the right $\Gamma_{25v} \rightarrow X_{1c}$ indirect gap (1.28 eV), and proper band alignment is obtained only for the full sp^3d^5 set (18 PAO). Comparing with other GW calculations, we find that our GW results agree well with those using 60 Gaussian orbitals [GW(60 GO)],⁴ or using plane wave functions [GW(PW)].³ Our results also closely resemble the experimental data,¹³ despite the lack of adjustable parameters.¹⁴

We then apply our approach to study the quasiparticle energy spectrum and the dielectric response functions of Si_{20} and Si_{60} clusters. The electronic and atomic structures of the clusters were obtained from the first-principles quantum molecular-dynamics method mentioned before.^{5,16} In the calculation of the electronic band structure, a larger basis of sp^3d^5 orbitals was employed.¹⁷ The atomic structures and the electronic density of states (EDOS) of the resulting Si_{20} and Si_{60} clusters are illustrated in Figs. 1–3. The lowest-energy ‘‘equilibrium’’ configuration of the Si_{20} cluster, obtained after annealing and quenching,¹⁶ is of a compact and closed-network type [see Fig. 1(a)], with no clear central atom group. On the other hand, the equilibrium configuration of the Si_{60} cluster [Fig. 1(b)] is slightly more oblate in shape than the Si_{20} cluster, and with several interior atoms exhibiting a degree of overcoordination. The difference in their structures is reflected on their EDOS, both in the shape of the EDOS, and also in the LDA band gap, giving quite different values, 1.12 in Si_{20} , and 0.55 eV in Si_{60} , respectively [see Figs. 2(a) and 3(a)]. Moreover, the annealing of the structure yields interesting spatially localized highest occupied molecular orbital and lowest unoccupied molecular orbital states and others near the gap.^{16,17}

In the quasiparticle calculation, we use supercells of $15 \times 15 \times 15$ Å³ for Si_{20} , and $20 \times 20 \times 20$ Å³ and Si_{60} .⁸ The transition matrix-elements $M_{\mathbf{G}}^{mn}(\mathbf{k}, \mathbf{q})$ were calculated using a Fourier representation with 850 \mathbf{G} vectors in reciprocal space, to achieve a good description within an accuracy of 10^{-2} . We find that, due to the complex products of matrix elements $M_{\mathbf{G}}^{mn}(\mathbf{k}, \mathbf{q})$ in expressions such as Eqs. (7)–(8), the

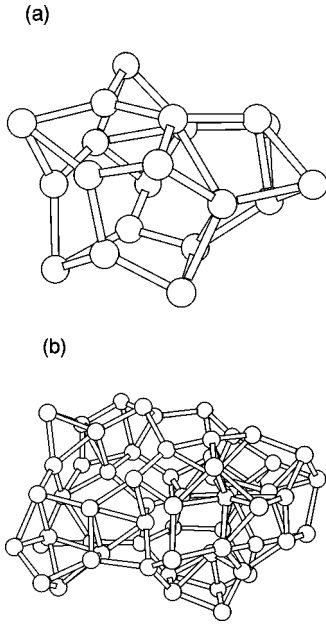


FIG. 1. (a) Lowest energy atomic structure of Si_{20} , and (b) Si_{60} .

cutoff energy and corresponding number of \mathbf{G} -vectors required are much lower than for the wave function $\psi_{n\mathbf{k}}(\mathbf{r})$ or the density $\rho(\mathbf{r})$. The symmetrized dielectric matrix element $\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}(\mathbf{q}, \omega)$ is computed according to Eq. (7) for the needed \mathbf{q} and ω . The inverse matrix $\tilde{\epsilon}_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}, \omega)$ is then obtained by numerical inversion. The ω' -integration in the second term of Eq. (8) is performed over a one-dimensional grid with 0.2 eV step, in a range of four times the bandwidth, large enough

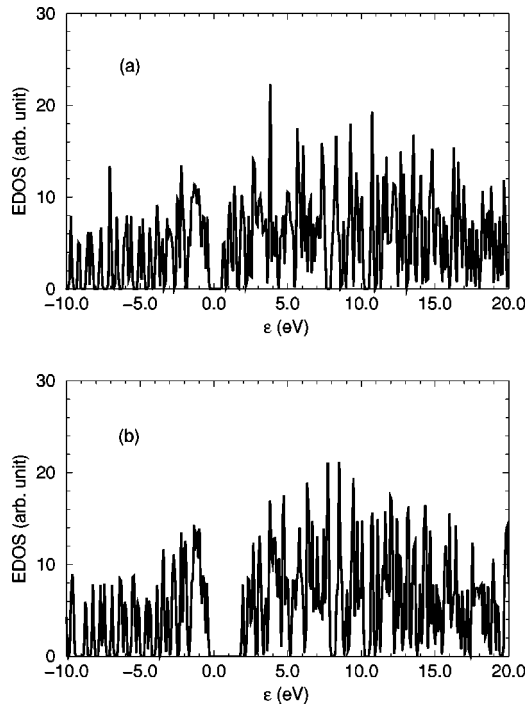


FIG. 2. (a) Electronic density of states of Si_{20} calculated using LDA with an sp^3d^5 basis. (b) The quasiparticle energy spectrum using the GW correction. The Fermi level is set at 0.0 eV. Level broadening is 0.05 eV.

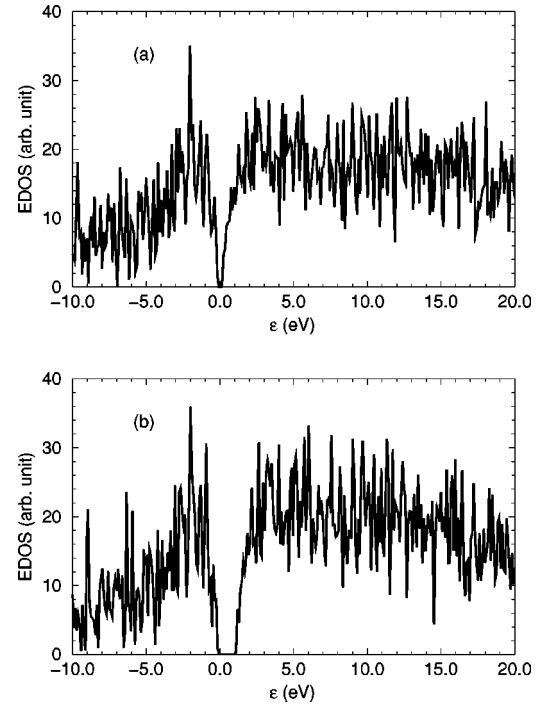


FIG. 3. (a) Electronic density of states of Si_{60} calculated using LDA with an sp^3d^5 basis. (b) The quasiparticle energy spectrum using the GW approximation. The Fermi level is set at 0.0 eV. Level broadening is 0.05 eV.

to achieve convergence. The pole structure along the real energy axis is regularized by an imaginary infinitesimal factor $i\eta$ ($\eta=0.1$ eV in the present calculation). The renormalization factor $Z_{n\mathbf{k}}$ is calculated numerically by a five-point derivative formula around each $\epsilon_{n\mathbf{k}}^{LDA}$. The resulting nearly-constant value of $Z_{n\mathbf{k}} \approx 0.85$ for most band energies in both clusters is in agreement with the typical assumption of a constant value made in the literature.¹⁸ The imaginary part of the self-energy operator is also analyzed to evaluate the lifetime of the quasiparticle. In all bands, except near the bottom of the valence band and the top of the conduction band (i.e., away from the gap), it has a magnitude of order 10^{-2} eV, showing the good stability of the quasiparticles for excitations close to the gap. The V^{xc} data used in Eq. (5) are taken from the local basis functional LDA results, which range from -11.7 to -9.9 eV in these clusters.

The calculated quasiparticle excitation spectrum for Si_{20} and Si_{60} clusters is presented in Figs. 2(b) and 3(b), respectively. In general, of course, the quasiparticle correction depends on the particular energy level and wave function considered. Compared to the LDA EDOS [Figs. 2(a) and 3(a)], we find that the quasiparticle energy spectrum remains more or less unchanged in shape as compared to LDA EDOS, except for a small enhancement near the valence band edge. On the other hand, the LDA conduction band energies are shifted to higher energies, opening the gap by about 1.3 eV in Si_{20} , and 0.9 eV in Si_{60} after the GW correction. The fundamental band gap of Si_{20} is then at 2.42 eV, and that of Si_{60} at 1.45 eV, for the larger sp^3d^5 basis (see Table II for other values).

We have also studied the sensitivity of the dielectric re-

TABLE II. Elemental gap for Si clusters at different approximations, all in eV.

Cluster	LDA (sp^3)	GW (sp^3)	LDA (sp^3d^5)	GW (sp^3d^5)
Si ₂₀	1.19	3.11	1.12	2.42
Si ₆₀	0.74	1.87	0.55	1.45

sponse function to quasiparticle corrections. Notice that the intercluster LF effect should disappear in the case of real isolated clusters (except for the intracluster terms explicitly considered here). In our simulation, we have placed the cluster into a cubic supercell, although it is large enough to ensure that each cluster is isolated (with no intercluster electron hopping).⁸ We have verified that the LF effect arising from possible long-range Coulomb interaction with the clusters in neighboring cells is indeed negligible on the dielectric function. Therefore, we have explicitly verified that $\epsilon^M(\omega) = \lim_{\mathbf{q} \rightarrow 0} \epsilon_{00}(\mathbf{q}, \omega)$, as we would anticipate of negligible ‘‘bulk’’ LF effects.¹¹ The imaginary part of the dielectric response function of the clusters in the energy region of interest is presented in Fig. 4, both before (dotted curves) 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 changed slightly near the first absorption peak, producing an overall smoothing and oscillator strength distribution. 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 ≈ 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.¹⁹

In Fig. 4, we show also the role of the plasmon pole approximation (dashed curves) vs the full frequency dependence calculations. It is clear in Fig. 4(b) that in Si₆₀, both GW calculations agree quite well. On the other hand, for Si₂₀, the plasmon pole approximation overestimates the gap correction by ≈ 0.3 eV, indicating that consideration of the full frequency dependence is important in these calculations. The good agreement in Fig. 4(b) is in accordance with the good behavior of the plasmon pole approximation seen in bulk calculations.³

In summary, we have developed an *ab initio* method to calculate the optical properties of semiconductors and insulators using a local basis set. The frequency dependence of the dielectric matrix elements is fully included in this GW calculation for clusters. We find that the GW corrections significantly enhance the optical gap by 1.3 eV in Si₂₀ and 0.9 eV in Si₆₀ from the LDA results. This influence is larger than in bulk Si, where a shift of ≈ 0.8 eV in the optical gap is found.²⁰ Such tendency to higher shifts was found also in the silicon nanocrystals studied by Ögüt *et al.*,²¹ probably as a consequence of quantum confinement of the electron due to the small cluster size. The quasiparticle energy spectrum has been obtained starting from the LDA band energies and wave functions in a nonself-consistent GW approach, as in the work by other groups.^{2,3} However, recent work on GW

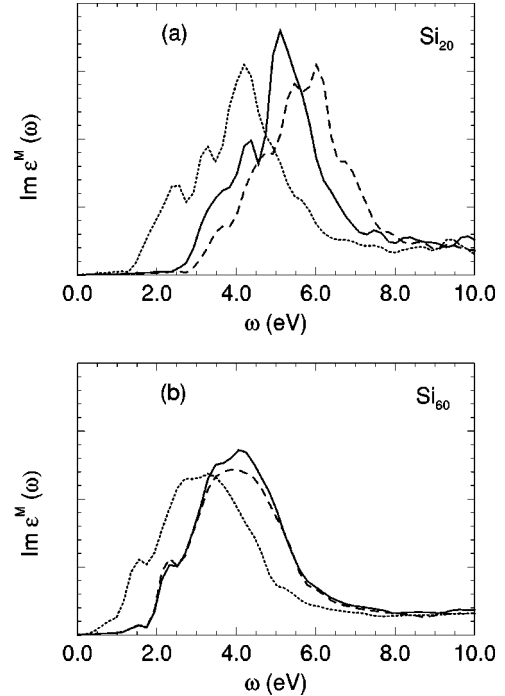


FIG. 4. Imaginary part (in arbitrary units) of the macroscopic dielectric function $\epsilon^M(\omega)$ for (a) Si₂₀, and (b) Si₆₀ clusters. The solid (dotted) curve indicates results after (before, LDA) GW corrections. Feature broadening in plot is 0.1 eV. Dashed traces in both panels are GW calculations with generalized plasma pole approximation, for comparison.

(Ref. 22) emphasizes that self-consistency is an important issue in GW calculations, to guarantee that the final results are independent of the starting Green’s function (see also discussion in Ref. 2). The disagreement with experiment of the self-consistent GW results for bulk Si (Ref. 22) implies that higher order vertex corrections beyond the simple GW followed here would have to be considered. To what extent these effects would impact on the dielectric response functions of Si₂₀ and Si₆₀ clusters and other systems is an important point deserving further consideration. Our local-basis approach should allow exploration of this and other related issues (such as LF in cluster arrays) from first principles, at a moderate computational cost. Moreover, excitonic effects related to the two-particle self-energy terms in the electron-hole interaction are found to be important in finite-size systems due to the weaker screening of the Coulomb interaction.²³ For Si nanocrystals, for example, the exciton effect reduces the band gap, corrected by GW, and gives an optical gap, which is in good agreement with experiments.²¹ Incorporation of these effects for Si₂₀ and Si₆₀ clusters, which may indeed contribute to the larger gaps we find here, remains as a future challenge in our formulation.

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- ¹L. Hedin, Phys. Rev. **139**, A796 (1965).
- ²F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998); W. G. Aulbur, L. Jönsson, and J. W. Wilkins, Solid State Phys., accepted (1999).
- ³M.S. Hybertsen and S.G. Louie, Phys. Rev. B **34**, 5390 (1986); J.E. Northrup, M.S. Hybertsen, and S.G. Louie, *ibid.* **39**, 8198 (1989); R.W. Godby, M. Schlüter, and L.J. Sham, *ibid.* **37**, 10 159 (1988).
- ⁴M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B **48**, 17 791 (1993); **52**, 1905 (1995).
- ⁵O.F. Sankey and D.J. Niklewski, Phys. Rev. B **40**, 3979 (1989); A.A. Demkov, J. Ortega, O.F. Sankey, and M.P. Grumbach, *ibid.* **52**, 1618 (1995).
- ⁶D. Sánchez-Portal, P. Ordejón, E. Artacho, and J.M. Soler, Int. J. Quantum Chem. **65**, 453 (1997).
- ⁷D. Sánchez-Portal, E. Artacho, and J.M. Soler, Solid State Commun. **95**, 685 (1995); J. Phys.: Condens. Matter **8**, 3859 (1996).
- ⁸As described below, the clusters are assembled in a large-period supercell structure to “allow” the use of the LDA approach (Ref. 5).
- ⁹D.M. Ceperley and G.J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- ¹⁰M. Yu, S. E. Ulloa, and D. A. Drabold (unpublished).
- ¹¹D.L. Johnson, Phys. Rev. B **9**, 4475 (1974); V.I. Gavrilenko and F. Bechsted, Phys. Rev. B **54**, 13 416 (1996); W.L. Mochan and R.G. Barrera, Phys. Rev. Lett. **56**, 2221 (1986).
- ¹²N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Saunder College Publishing (Harcourt Brace College Publishers, New York, 1976).
- ¹³*Numerical Data and Functional Relationships in Science and Technology*, edited by K. H. Hellwege and O. Madelung, Landolt-Börnstein, New Series, Group III, Vols. **17a** and **22a** (Springer, Berlin, 1982).
- ¹⁴For the bulk calculation, we have used the von der Linden-Horsch plasmon-pole model (Ref. 15), for ease of calculation and to provide better comparison with previous results in Table I.
- ¹⁵W. von der Linden and P. Horsch, Phys. Rev. B **37**, 8351 (1988).
- ¹⁶J. Song, S.E. Ulloa, and D.A. Drabold, Phys. Rev. B **53**, 8042 (1996).
- ¹⁷C. Noguez, J. Song, S.E. Ulloa, D.A. Drabold, and S.H. Yang, Superlattices Microstruct. **20**, 405 (1996).
- ¹⁸W. G. Aulbur, Ph.D. thesis, The Ohio State University (1996).
- ¹⁹T. Shimizu-Iwayama, N. Kurumado, D.E. Hole, and P.D. Townsend, J. Appl. Phys. **83**, 6018 (1998).
- ²⁰B. Delley and E.F. Steigmeier, Phys. Rev. B **47**, 1397 (1993); Appl. Phys. Lett. **67**, 2370 (1995).
- ²¹S. Ögüt, J.R. Chelikowsky, and S.G. Louie, Phys. Rev. Lett. **79**, 1770 (1997); M. Rohlfing and S.G. Louie, *ibid.* **80**, 3320 (1998).
- ²²W.D. Schöne and A.G. Eguiluz, Phys. Rev. Lett. **81**, 1662 (1998).
- ²³M. Rohlfing and S.G. Louie, Phys. Rev. Lett. **81**, 2312 (1998); S. Albrecht, L. Reining, R. Del Sole, and G. Onida, *ibid.* **80**, 4510 (1998).