Ab Initio Calculations for Large Dielectric Matrices of Confined Systems

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Abstract

Calculations for optical excitations in confined systems require knowledge of the inverse screening dielectric function $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$, which plays a crucial role in determining screened Coulomb potentials and exciton binding energies. We present a new efficient real-space method of inverting and storing large dielectric matrices (of dimension $N > 10^4$) for confined systems from first principles. The method relies on the separability of ϵ matrix in $\mathbf{r}$ and $\mathbf{r}'$ by expressing it as a sum of the identity matrix and an outer product of two low-rank matrices. The method has allowed, for the first time, full *ab initio* calculation of $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$ of dimension $N \sim 270,000$, and for quantum dots as large as $Si_{35}H_{36}$. The effective screening in Si quantum dots up to 1.1 nm in diameter is found to be very ineffective with average dielectric constants ranging from 1.1 in SiH_4 to 1.4 in $Si_{35}H_{36}$.

Optical excitations in confined systems differ greatly from those in extended systems due to quantum confinement and surface effects. For example, the 1.17 eV band gap of bulk Si increases to several volts in Si_nH_m nanocrystals. Over the last decade, there has been a great deal of interest in accurate calculations of excitation energies in such important nanostructures as hydrogenated silicon clusters as well as other confined semiconductor quantum dots [1–12]. The first step in the calculation of the optical gap usually involves the calculation of the quasiparticle gap, which is the energy needed to create a non-interacting electron-hole pair. The second component is due to the direct Coulomb (E_{Coul}) and exchange (E_{ex}) electron-hole interactions comprising the exciton binding energy. While this second term is quite negligible in bulk materials (~ 15 meV in crystalline Si), its value can increase by one to two orders of magnitude, hence become comparable to the quasiparticle gaps for nanoscale quantum structures [4, 5, 10]. This is due to both the increase of the unscreened Coulomb energy in confined systems and the decrease in effective medium screening. As a result, it is necessary to calculate exciton binding energies accurately in confined systems. An important part of such calculations involves obtaining the inverse screening dielectric matrix $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$, which plays a crucial role in determining the magnitude of the screened exciton Coulomb potential and energy.

The calculation of the full inverse screening dielectric matrix $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$ from first principles is computationally very demanding for confined systems. As a result, earlier approaches to estimating the exciton Coulomb energy in a Si quantum dot have used drastic approximations such as the static dielectric constant of either bulk Si [13, 14] or the quantum dot itself [12, 15]. More recent studies have incorporated the spatial dependence of screening inside a quantum dot by using position-dependent model dielectric functions within generalized Penn [11] or Thomas-Fermi models [16], as well as a tight-binding approach [17]. The two main difficulties associated with *ab initio* calculations of the full $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$ arise in the inversion of ϵ and in calculations of such functions as $g(\mathbf{r}, \mathbf{r}'') = \int d\mathbf{r}' \epsilon^{-1}(\mathbf{r}, \mathbf{r}') f(\mathbf{r}', \mathbf{r}'')$. Both of these operations scale as N^3, where N is the number of grid points. In addition, storing the entire ϵ or ϵ^{-1} matrix may not be possible due to memory requirement when N is large, as is the case for confined systems. In this paper, we present an efficient method of obtaining and storing *ab initio* $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$ for confined systems. We use the method to calculate perturbatively the exciton Coulomb energies in hydrogenated Si quantum dots as large as $Si_{35}H_{36}$. For all the quantum dots studied, we find very ineffective screening of the electron-hole

Coulomb interaction. Our results help formulate possible model dielectric functions for such confined systems based on *ab initio* calculations of the full dielectric matrix.

The ground state, dielectric matrix, and exciton Coulomb energy calculations presented in this paper were performed in real space. For ground state calculations within the local density approximation, a higher-order finite-difference *ab initio* pseudopotential method was used [18]. The clusters considered in this study, SiH_4, Si_2H_6, Si_5H_{12}, $Si_{10}H_{16}$, $Si_{14}H_{20}$, and $Si_{35}H_{36}$, were generated as bulk Si fragments, and the Si−Si and Si−H bondlengths were optimized by minimizing the quantum forces. The sensitivity of the results with respect to three important parameters, the grid spacing h, the radius R of the physical domain outside which the wavefunctions are required to vanish, and the number of unoccupied states N_c included in the band summations in ϵ calculations, were carefully tested for each case. The radius R of the physical domain was the most important parameter for calculations of the exciton Coulomb energy E_{Coul}, especially for smaller clusters. For example, although the effective radius of SiH_4 is ~ 2 Å, both the screened and unscreened E_{Coul} reach a convergence of 0.1 eV only for $R \sim 20 - 25$ Å, as shown in Fig. 1. This is mainly related to the slow convergence of the lowest unoccupied molecular orbital (LUMO) as a function of the physical domain size. Another manifestation of this slow convergence is the spurious negative electron affinity calculated for small Si_nH_m clusters embedded in not-large-enough domain sizes [4, 5]. All relevant physical parameters used in the calculations are shown in Table I.

After obtaining the highest occupied molecular orbital (HOMO) and LUMO from the ground state calculation, the exciton Coulomb energy E_{Coul} can be written in a first-order perturbative formalism as

$$
\begin{aligned}
E_{\mathrm{Coul}} &= \int d\mathbf{r_1} |\psi_e(\mathbf{r_1})|^2 V_{\mathrm{scr}}^{\mathrm{h}}(\mathbf{r_1}) \\
&= \int d\mathbf{r_1} |\psi_e(\mathbf{r_1})|^2 \int d\mathbf{r} \epsilon^{-1}(\mathbf{r_1},\mathbf{r}) V_{\mathrm{unscr}}^{\mathrm{h}}(\mathbf{r}) \\
&= \iiint \epsilon^{-1}(\mathbf{r_1},\mathbf{r}) \frac{|\psi_e(\mathbf{r_1})|^2 |\psi_h(\mathbf{r_2})|^2}{|\mathbf{r}-\mathbf{r_2}|} d\mathbf{r} d\mathbf{r_1} d\mathbf{r_2}.
\end{aligned} \tag{1}
$$

In this expression, $V_{\mathrm{scr}}^{\mathrm{h}}$ and $V_{\mathrm{unscr}}^{\mathrm{h}}$ are screened and unscreened potentials due to the hole, ψ_e and ψ_h are the electron (LUMO) and hole (HOMO) wavefunctions, and ϵ^{-1} is the inverse of the static dielectric matrix. If we formally define $\tilde{\epsilon}^{-1}$ as

$$
\int \epsilon^{-1}(\mathbf{r_1},\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r_2}|} d\mathbf{r} \equiv \tilde{\epsilon}^{-1}(\mathbf{r_1},\mathbf{r_2}) \frac{1}{|\mathbf{r_1}-\mathbf{r_2}|}, \tag{2}
$$

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then the exciton Coulomb energy can be written as

$$E_{\text{Coul}} = \iint \tilde{\epsilon}^{-1}(\mathbf{r_1}, \mathbf{r_2}) \frac{|\psi_e(\mathbf{r_1})|^2 |\psi_h(\mathbf{r_2})|^2}{|\mathbf{r_1} - \mathbf{r_2}|} d\mathbf{r_1} d\mathbf{r_2}. \tag{3}$$

As a first step in computing E_{Coul} from Eq. (3), $\epsilon(\mathbf{r}, \mathbf{r}')$ needs to be calculated. Within density functional linear response theory, ϵ can be shown to have the following form [19]:

$$\epsilon(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') - \int d\mathbf{r_1} \left[\frac{1}{|\mathbf{r} - \mathbf{r_1}|} + \frac{\delta^2 E_{\text{xc}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r_1})} \right] \chi_0(\mathbf{r_1}, \mathbf{r}') \tag{4}$$

where E_{xc} is the exchange-correlation functional, and $\chi_0(\mathbf{r}, \mathbf{r}')$ is the independent particle polarizability:

$$\chi_0(\mathbf{r}, \mathbf{r}') = \sum_{i,j} (f_i - f_j) \frac{\psi_i^*(\mathbf{r})\psi_j(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_j} \tag{5}$$

as expressed in terms of the Kohn-Sham wavefunctions $\psi_i(\mathbf{r})$, the Kohn-Sham eigenvalues ε_i and occupation numbers f_i. With real wavefunctions and integer occupation numbers (as suitable for confined semiconductor systems), the expression for the static dielectric response function can be simplified by also taking spin-degeneracy into account as

$$\epsilon(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') + 4 \sum_{v,c} (J_{vc}(\mathbf{r}) + K_{vc}(\mathbf{r})) \frac{\psi_v(\mathbf{r}')\psi_c(\mathbf{r}')}{\varepsilon_c - \varepsilon_v} \tag{6}$$

where the summations v, c are over the valence and conduction orbitals, and the integrals $J_{vc}(\mathbf{r})$ and $K_{vc}(\mathbf{r})$ are defined as

$$J_{vc}(\mathbf{r}) = \int d\mathbf{r_1} \frac{\psi_v(\mathbf{r_1})\psi_c(\mathbf{r_1})}{|\mathbf{r} - \mathbf{r_1}|} \tag{7}$$

$$K_{vc}(\mathbf{r}) = \int d\mathbf{r_1} \frac{\delta^2 E_{\text{xc}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r_1})} \psi_v(\mathbf{r_1})\psi_c(\mathbf{r_1}) = \frac{\delta^2 E_{\text{xc}}}{\delta\rho^2(\mathbf{r})} \psi_v(\mathbf{r})\psi_c(\mathbf{r}) \tag{8}$$

For calculating exciton Coulomb energies and many other physical quantities, the inverse of the $\epsilon(\mathbf{r}, \mathbf{r}')$ matrix is needed. As mentioned earlier, in terms of computational cost, this matrix inversion scales as N^3 (N is the total number of grid points in the physical domain). In addition, the storage required by the full matrix naturally scales as N^2. Both the computational cost and the storage requirement become critical problems above $N \sim 10^4$. The form of the dielectric response function in Eq. (6) allows us to reduce this computational cost and storage requirement significantly by observing that $\epsilon(\mathbf{r}, \mathbf{r}')$ is separable in $\mathbf{r}$ and $\mathbf{r}'$. This makes it possible to express the matrix ϵ in terms of identity matrix I and rank $N_{vc} = N_v \times N_c$ matrices U and V, where N_v and N_c are the number of valence and conduction

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orbitals, respectively. The matrices U and V are defined as $U = 2(J_{vc} + K_{vc})$ and $V = 2\psi_v\psi_c/(\varepsilon_c - \varepsilon_v)$ for which the rows are labeled (from 1 to N) by grid points, and the columns are labeled (from 1 to N_{vc}) by valence and conduction orbital pairs. This leads to the following matrix expression for the response function,

$$\epsilon = I + UV^T, \tag{9}$$

where V^T is the transpose of matrix V. Expressing the ϵ matrix in this fashion allows us to calculate its inverse in terms of the inverse of the matrix $X = I + V^T U$ as follows:

$$\epsilon^{-1} = (I + UV^T)^{-1} = I - UX^{-1}V^T \tag{10}$$

On a Cartesian grid of uniform spacing h, the elements of the inverse dielectric matrix can finally be written as

$$\epsilon_{ij}^{-1} = \frac{1}{h^3}\left(\delta_{ij} - \sum_{k,l=1}^{N_{vc}} U_{ik}X_{kl}^{-1}V_{lj}^T\right). \tag{11}$$

We note that X is a $N_{vc} \times N_{vc}$ matrix, which implies that compared to direct inversion of the ϵ matrix, this method of finding ϵ^{-1} is faster by a factor of $(N/N_{vc})^3$, which can be as large as several orders of magnitude depending on the physical domain size, the grid spacing h, and the number of occupied orbitals. In addition, the full $\epsilon(\mathbf{r}, \mathbf{r}')$ or $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$ no longer needs to be stored. Instead, two $N \times N_{vc} < N^2$ arrays (U and V) need to be saved. Another advantage of the separability of ϵ is in the calculation of functions $g(\mathbf{r}, \mathbf{r}'') = \int d\mathbf{r}'\epsilon^{-1}(\mathbf{r}, \mathbf{r}')f(\mathbf{r}', \mathbf{r}'')$. The calculation of the effective screening function $\tilde{\epsilon}^{-1}(\mathbf{r_1}, \mathbf{r_2})$ in Eq. (2) is one example. Even if one were able to store the entire ϵ^{-1} matrix, the calculation of $\tilde{\epsilon}^{-1}$ would still be an N^3 operation. With the current expression in Eq. (11), this operation can be performed with two matrix-vector multiplications and scales as $N_{vc}N^2$. A striking example of the savings in computational time and memory can be given for the case of SiH$_4$. Due to convergence problems associated with the LUMO of this cluster as mentioned above, we used a domain size of $R = 20$ a.u, a grid spacing of $h = 0.5$ a.u, and $N_c = 26$ unoccupied states. This results in an ϵ matrix of dimension $N \sim 270,000$ and $N_{vc} = 104$. Storing the entire ϵ matrix would require ~ 600 GB of memory. Its direct inversion and calculation of E_{Coul} from Eq. (1) would take ~ 16 years on a 375 MHz Power3 processor. Instead, the new method requires a modest 450 MB of memory and takes ~ 40 hours on the same machine.

The calculated exciton Coulomb and binding energies $E_b = E_{\mathrm{Coul}} - E_{\mathrm{ex}}$ for all clusters considered are shown in Table II, along with spin-triplet excitation values from Quantum

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Monte Carlo (QMC) and GW-Bethe-Salpeter (GW-BS) calculations [4, 5]. Also shown are the average effective dielectric constants ϵ_{ave} defined as the ratio of the unscreened Coulomb energy to the screened Coulomb energy [$\epsilon_{\mathrm{ave}} = E_{\mathrm{Coul}}(\epsilon = 1)/E_{\mathrm{Coul}}$]. As expected, the unscreened Coulomb energies are quite large due to quantum confinement, ranging from about 5 eV in silane to 3.2 eV for a quantum dot of diameter 1.1 nm ($Si_{35}H_{36}$). Furthermore, we find that the screening in these quantum dots is very ineffective, as demonstrated by the large values of screened exciton Coulomb energies in Table II. Although ϵ_{ave} increases steadily in going from SiH_4 to $Si_{35}H_{36}$ (as expected from quantum confinement models), the actual values of ϵ_{ave} (from 1.1 to 1.4) are very small compared with the bulk dielectric constant of 11.4. Comparison of the exciton Coulomb energies with binding energies E_b shows, as expected, that the attractive direct Coulomb interaction is at least one order of magnitude than the repulsive exchange interaction. Finally, the results obtained using the simple perturbative formalism of Eq. (1) agree very well with exciton binding energies for spin-triplet excitations calculated from the more sophisticated QMC and GW-BS formalisms.

We also examined the spatial variation of the screening function $\tilde{\epsilon}^{-1}(\mathbf{r_1}, \mathbf{r_2})$ in order to address dielectric screening in quantum dots with better empirical models based on *ab initio* calculations. Clearly, a computationally convenient model dielectric function is one that depends only on the particle separation $r = |\mathbf{r_1} - \mathbf{r_2}|$. We therefore set $\mathbf{r_1} = \mathbf{0}$, and plotted $1/\tilde{\epsilon}^{-1}(\mathbf{0}, \mathbf{r_2})$ as a function of the distance from the origin. Since the actual $\tilde{\epsilon}$ is not spherically symmetric (only the symmetry-related positions have the same value), we averaged $\tilde{\epsilon}^{-1}(\mathbf{0}, \mathbf{r_2})$ over the positions $\mathbf{r_2}$ with $|\mathbf{r_2}| = r$. The resulting function $\bar{\epsilon}(r) = 1/\tilde{\epsilon}^{-1}(0, r)$ is plotted in Fig. 2 for SiH_4, Si_5H_{12}, and $Si_{35}H_{36}$ quantum dots. The effective screening functions $\bar{\epsilon}(r)$ are seen to increase rapidly and peak at a distance typically smaller than the effective radius of the quantum dot. After this peak, the screening function $\bar{\epsilon}(r)$ approaches unity, as it should, since the quantum dot is in vacuum. This type of behavior is substantially different from those predicted by empirical Thomas-Fermi model dielectric screening functions used in some earlier calculations. For example, the extension of Resta's model (developed for *bulk* semiconductors) [20] to quantum dots [16] results in an effective $\bar{\epsilon}(r)$ that becomes equal to the static dielectric constant of the quantum dots outside a radius R_{∞}. When such models are used in exciton Coulomb energy calculations, they predict much smaller exciton Coulomb energies than those calculated from *ab initio* screening dielectric matrices [21]. In addition, since these models treat the quantum dot as a homogeneous region outside of R_{∞},

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it becomes necessary to take into account extra empirical terms due to surface polarization [16, 17, 22]. Our method, which makes it possible to obtain the full inverse dielectric matrix, avoids all these problems, and results in large exciton Coulomb energies due to ineffective screening inside the quantum dot and the presence of a surface.

We have observed that $\bar{\epsilon}(r)$ obtained from our *ab initio* calculations can be fitted quite well to a two-parameter model function of the form $\epsilon_m(r) = 1 + \alpha r^2 e^{-\beta r}$. The calculated parameters α and β for various quantum dots and the resulting exciton Coulomb energies calculated with the model functions are given in Table III. As seen in this table, the E_{Coul}^m values calculated from the $\epsilon_m(r)$ fall within 5 % of the *ab initio* values. Given the approximations made in obtaining the model function (such as radial averaging and only distance-dependence of $\bar{\epsilon}$), this agreement with *ab initio* results is quite good, and promising for future studies of efficient and accurate model dielectric functions for confined systems.

In summary, we have presented a new efficient way of inverting and storing large dielectric matrices $\epsilon(\mathbf{r}, \mathbf{r}')$ of confined nanostructures from first principles using the separability of ϵ in $\mathbf{r}$ and $\mathbf{r}'$. This has allowed us for the first time to calculate perturbatively the *ab initio* exciton Coulomb energies of Si quantum dots up to 1.1 nm in diameter, as well as $\epsilon^{-1}(\mathbf{r}, \mathbf{r}')$ matrices with dimensions of several hundred thousands. We found that the screening in small Si quantum dots is very ineffective with average dielectric constants ranging from 1.1 in silane to ~ 1.4 in $Si_{35}H_{36}$. New distance-dependent model dielectric screening functions fitted to *ab initio* calculations give good results for exciton Coulomb energies. Such model dielectric functions based on *ab initio* results should be very useful for efficient and accurate studies of excited state electronic structure and response functions in nanocrystals.

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FIG. 1: The unscreened ($\diamondsuit$) and screened ($\square$) exciton Coulomb energies of SiH_4 as a function of the radius R of the spherical domain. The Si atom is placed at the center of the sphere. For this calculation, the grid spacing h and the number of unoccupied states N_c were set to 0.8 a.u. and 16, respectively. The difference of the asymptotic values from the fully converged ones in Table II is due to the fact that the energies shown here are not converged with respect to h and N_c.

FIG. 2: The averaged screening functions $\overline{\epsilon}(r) = 1/\tilde{\epsilon}^{-1}(0, r)$ for the three quantum dots SiH_4, Si_5H_{12}, and $Si_{35}H_{36}$. Their effective radii are 1.7 Å, 2.9 Å, and 5.5 Å, respectively.

TABLE II: Calculated unscreened $[E_{\text{Coul}}(\epsilon = 1)]$ and screened exciton Coulomb energies, exciton binding energies E_b, average dielectric constants ϵ_{ave} (defined in the text), and exciton binding energies calculated using QMC and GW-BSE methods. All energies are in eV.

Cluster	E_{Coul} ($\epsilon = 1$)	E_{Coul}	ϵ_{ave}	E_b	QMC,GW-BS
SiH_4	5.06	4.50	1.12	4.28	4.3-4.4
Si_2H_6	4.90	4.22	1.16	4.04	4.10
Si_5H_{12}	4.80	3.87	1.24	3.65	3.55
$Si_{10}H_{16}$	4.20	3.31	1.27	3.10	3.35
$Si_{14}H_{20}$	3.79	2.96	1.28	2.83	—
$Si_{35}H_{36}$	3.17	2.38	1.33	2.30	—

TABLE I: Grid spacing h (in a.u.), radius R (in a.u.) of the domain in which the cluster is placed, the Hamiltonian dimension N, and the number of valence-conduction orbital pairs (N_{vc}) used in the calculations.

Cluster	h	R	N	N_{vc}
SiH_4	0.5	20	267,761	104
Si_2H_6	0.6	16	79,501	280
Si_5H_{12}	0.6	16	79,501	864
$Si_{10}H_{16}$	0.6	14	52,971	1,456
$Si_{14}H_{20}$	0.6	14	52,971	2,698
$Si_{35}H_{36}$	0.8	17.5	43,819	8,800

TABLE III: Parameters α and β obtained by fitting averaged dielectric function $\bar{\epsilon}(r) = 1/\tilde{\epsilon}^{-1}(0,r)$ to a model function $\epsilon_m(r) = 1 + \alpha r^2 e^{-\beta r}$. E_{Coul} and E_{Coul}^m are the calculated exciton Coulomb energies (in eV) using the *ab initio* $\epsilon(\mathbf{r}, \mathbf{r}')$ and the model $\epsilon_m(r)$, respectively.

Cluster	α (a.u.$^{-2}$)	β (a.u.$^{-1}$)	E_{Coul}	E_{Coul}^m
SiH_4	0.73	1.13	4.50	4.67
Si_5H_{12}	1.47	0.92	3.87	3.68
$Si_{35}H_{36}$	1.49	0.71	2.38	2.33