

Calculating the density of states and optical-absorption spectra of large quantum systems by the plane-wave moments method

Lin-Wang Wang

National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 22 November 1993; revised manuscript received 27 December 1993)

The moments method is used to calculate the density of states and optical-absorption spectra of large quantum systems. This method uses random wave functions to calculate 500 Chebyshev moments of the density of states (500^2 for the optical-absorption spectra), and transforms these moments back to energy space. The results compare well with direct calculations on a large, 2048 Si-atom bulklike supercell system. To demonstrate its utility, the spectra of a realistic quantum dot with 1035 Si and 452 H atoms are calculated using an empirical pseudopotential Hamiltonian and a plane-wave basis of wave functions.

Present solid-state electronic-structure calculations can be divided into two categories. In the first, one is interested in predicting atomic positions or the dynamics of atomic motions, thus the total energy and all occupied levels of the system are needed.¹ In the second, one is interested in some electronic properties at a fixed geometry, e.g., the band gap, the density of states (DOS), and the optical-absorption spectra (OAS). In this paper I address the second class of problems, especially for the cases where the Hamiltonian can be reliably approximated by a non-self-consistent form. Current electronic-structure methods using plane-wave bases are not capable of calculating large systems with thousands of atoms due to their N^3 scaling,² where N is the size of the system. In a previous paper,³ Zunger and I presented a method to calculate the *band-gap edge states* for such systems. The method of the present paper is complementary in that it can be used to calculate the DOS and OAS. Combining these two methods, most optical properties of a thousand-atom system can be calculated using a plane-wave basis for the wave functions and empirical pseudopotentials for the Hamiltonians.

In the generalized moments approach for the calculation of the DOS Refs. (4–8), one first calculates the generalized *moments* of the DOS $\rho(E)$,

$$I_n \equiv \int_{-1}^1 T_n(E) \rho(E) dE, \quad (1)$$

where $T_n(E)$ is a polynomial of power n defined in the interval $[-1:1]$, and the energy of the Hamiltonian has been scaled and shifted, so that all its eigenvalues are inside $[-1:1]$. Throughout this paper, the Chebyshev polynomial $T_n(x)$ will be used. It is chosen because it is an orthogonal polynomial and its linear transformations from I_n to $\rho(E)$ is a disguised Fourier transformation, thus fast Fourier transformation (FFT) can be used later. The Chebyshev polynomial is defined in $[-1:1]$ as

$$\begin{aligned} T_0(x) &= 1, \quad T_1(x) = x, \\ T_n(x) &= 2xT_{n-1}(x) - T_{n-2}(x). \end{aligned} \quad (2)$$

It has the orthogonality relation⁹

$$\int_{-1}^1 T_m(x) T_n(x) (1-x^2)^{-1/2} dx = \frac{\pi}{2} \delta_{nm} (1 + \delta_{m0}). \quad (3)$$

Following Eqs. (3) and (1), $\rho(E)$ can be reconstructed from I_n as

$$\rho(E) = \frac{2}{\pi} (1-E^2)^{-1/2} \sum_n T_n(E) I_n (1 + \delta_{n0})^{-1}. \quad (4)$$

Following Skilling,¹⁰ I will use statistical means to calculate $\{I_n\}$. First, assume that the Hamiltonian \hat{H} has N eigenstates $\{\phi_i\}$ and eigenvalues $\{E_i\}$ under the basis used. A random wave function ψ_0 can be generated by using a linear combination of an arbitrary orthonormal basis $\{\chi_i\}$ with random coefficients $\{b_i\}$, i.e., $\psi_0 = \sum_i b_i \chi_i$. Because the transformation from $\{\chi_i\}$ to the eigenstates $\{\phi_i\}$ is unitary, we can rewrite ψ_0 as

$$\psi_0 = \sum_i b_i \chi_i = \sum_i a_i \phi_i, \quad (5)$$

and $\{a_i\}$ are random numbers just like $\{b_i\}$ with equal statistical means and zero correlations among them, i.e.,

$$\langle a_i^* a_j \rangle = \delta_{i,j}, \quad (6)$$

where $\langle \rangle$ denotes average over different random wave functions. (I have normalized the wave functions to N to simplify the following notation.) Following the recursion formula of Eq. (2), one can apply \hat{H} to the wave functions to generate ψ_n :

$$\hat{H} \psi_0 = \psi_1, \quad 2\hat{H} \psi_{n-1} - \psi_{n-2} = T_n(\hat{H}) \psi_0 = \psi_n. \quad (7)$$

Now, taking the products, we have

$$I'_n = 2 \langle \psi_0 | \psi_n \rangle = 2 \sum_i T_n(E_i) |a_i|^2. \quad (8)$$

If we use many random wave functions $\{\psi_0\}$, repeating the above process and taking the average of I'_n , we have

$$\langle I'_n \rangle = 2 \sum_i T_n(E_i) = \int_{-1}^1 T_n(E) \rho(E) dE, \quad (9)$$

where we have used Eq. (6) and $\rho(E) \equiv 2 \sum_i \delta(E - E_i)$, assuming double occupations. We see that $\langle I'_n \rangle$ approaches I_n when we sample a sufficiently large number of the random wave functions. The computational effort in this procedure involves N_c applications of \hat{H} to the wave functions (N_c is the maximum number of Chebyshev moments used here) multiplied by the number N_a

of random wave function averages. In this study, I have used $N_c = 500$ and $N_a = 20$. For reasons to be discussed later, the larger the system is, the smaller N_a needs to be in order to achieve the same statistical accuracy. This makes the present scheme scale with respect to the system's size, almost like a constant.

The above formula is for the total DOS. It can be easily changed to calculate related spectral functions. For example, to calculate the projected DOS on a given function χ , i.e., $\rho_p(E) \equiv 2 \sum_i \delta(E - E_i) |\langle \phi_i | \chi \rangle|^2$, simply replace the random wave function ψ_0 by χ and repeat the above operations without averaging. To calculate a local DOS defined by a weighting function $f(r)$, i.e.,

$$\rho_l(E) \equiv 2 \sum_i \delta(E - E_i) \int |\phi_i(r)|^2 f(r) d^3r,$$

replace the product in Eq. (8) by $2 \langle \psi_0 | f | \psi_n \rangle$ and keep everything else the same.

In order to calculate the optical-absorption spectra, one needs to calculate a two-dimensional function

$$\tau(E_1, E_2) \equiv \sum_{i,j} |\langle \phi_i | \hat{p} | \phi_j \rangle|^2 \delta(E_1 - E_i) \delta(E_2 - E_j), \quad (10)$$

where $|\langle \phi_i | \hat{p} | \phi_j \rangle|^2$ is the transition probability between state ϕ_i and ϕ_j , and \hat{p} is the momentum operator $i\hbar\nabla$. After $\tau(E_1, E_2)$ is obtained, the imaginary part of the dielectric constant $\epsilon_2(E)$ (proportional to the OAS by a volume factor) can be calculated by

$$\epsilon_2(E) = \alpha \int_{-\infty}^{E_f} dE_2 \int_{E_f}^{\infty} dE_1 \tau(E_1, E_2) \delta[E - (E_1 - E_2)], \quad (11)$$

where E_f is the Fermi energy and $\alpha = 8\pi^2 e^2 \hbar^2 / 3m^2 E^2 V$, where V is the volume of the system.

To calculate $\tau(E_1, E_2)$, we will first calculate the two-dimensional generalized moments of it. We first generate a random wave function ψ_0 as before [Eq. (5)], then calculate

$$\begin{aligned} \Lambda'_{n,m} &\equiv \langle \psi_0 | \hat{p} T_n(\hat{H}) \cdot \hat{p} T_m(\hat{H}) | \psi_0 \rangle \\ &= \sum_{i,j,l} a_i^* a_j T_n(E_i) T_m(E_j) \langle \phi_i | \hat{p} | \phi_l \rangle \cdot \langle \phi_l | \hat{p} | \phi_j \rangle. \end{aligned} \quad (12)$$

Now, repeat the above products with different random wave functions ψ_0 and average them. This gives

$$\begin{aligned} \Lambda_{n,m} &\equiv \langle \Lambda'_{n,m} \rangle = \sum_{i,j} T_n(E_i) T_m(E_j) |\langle \phi_i | \hat{p} | \phi_j \rangle|^2 \\ &= \int_{-1}^1 dE_1 \int_{-1}^1 dE_2 T_n(E_1) T_m \\ &\quad \times (E_2) \tau(E_1, E_2), \end{aligned} \quad (13)$$

where I have used Eqs. (6) and (10). After obtaining $\Lambda_{n,m}$, the reconstruction of $\tau(E_1, E_2)$ using Eq. (3) is straightforward,

$$\begin{aligned} \tau(E_1, E_2) &= \left[\frac{2}{\pi} \right]^2 (1 - E_1^2)^{-1/2} (1 - E_2^2)^{-1/2} \\ &\quad \times \sum_{n,m} T_n(E_1) T_m(E_2) \Lambda_{n,m} (1 + \delta_{n0})^{-1} \\ &\quad \times (1 + \delta_{m0})^{-1}. \end{aligned} \quad (14)$$

The calculation of Eq. (12) is carried out by first calculating $\psi_m = T_m(\hat{H})\psi_0$ as defined in Eq. (7) (computationally, ψ_m can be stored on disk space). Then $\psi_n^p(k) \equiv T_n(\hat{H})\hat{p}_k\psi_0$ are calculated using the same recursion relation as in Eq. (7). Here, k stands for the directions x, y, z (usually, by symmetry, only one or two k need to be calculated). The $\Lambda'_{n,m}$ is then $\sum_k \langle \psi_n^p(k) | \hat{p}_k | \psi_m \rangle$. [Note that $\psi_n^p(k)$ need not to be stored. The product is calculated right after each $\psi_n^p(k)$ is generated.] The computational effort to get $\Lambda_{n,m}$ is in the same order of the effort to get I_n , differing by a factor of two or more depending on how many \hat{p}_k need to be calculated. Besides, I_n (thus the DOS) can be calculated when one calculates $\Lambda_{n,m}$ essentially without any extra work. In Eq. (14), there are 500×500 $\Lambda_{n,m}$ values, thus the direct implementation of that equation can be a problem, because it is proportional to $(500 \times 500)^2$ operations. However, $T_n(E) = \cos(n\theta)$ and $\theta = \cos^{-1}(E)$.⁹ Substituting this into Eq. (14), we get a Fourier transformation for that equation. Thus, an FFT can be used to carry out the equation. After this step, the calculation of Eq. (14) takes only a small fraction ($< 1\%$) of the time of the whole calculation. The most time-consuming part in the whole procedure is the computation of $\Lambda_{n,m}$, and it is dominated by the computation of ψ_m and $\psi_n^p(k)$, via Eq. (7). The product $\sum_k \langle \psi_n^p(k) | \hat{p}_k | \psi_m \rangle$ takes less than $\frac{1}{4}$ of the total computational time.

Now I will give a few details and remarks about the current method.

(1) The resolution ΔE of a constructed spectrum is roughly $2/N_c$ for a given total number N_c of Chebyshev moments. The error of the statistical average (i.e., the fluctuation of the spectral height at a given point) is proportional to the inverse square root of $\Delta N \times N_a$, where ΔN is the number of eigenstates inside one ΔE . Because ΔN inside a fixed ΔE interval is roughly proportional to the size of the system, N_a should be inversely proportional to the size in order to give the same statistical accuracy for different system sizes. This, as mentioned earlier, yields a roughly constant scaling with the size of the system. This constant scaling changes to a linear scaling when the system is larger than a limit after which $N_a = 1$. This limit can be larger than 10 000 atoms. The conventional direct diagonalization method for obtaining the OAS scales as N^3 of the system's size N . The approximate crossover system size after which the current method becomes faster than the conventional one, is about 70 atoms, for the same spectrum resolution and statistical accuracy as we have in this paper.

(2) To reduce the noise in the statistical average, $(\hat{H} - E_c)^2$ has been applied to Eqs. (8) and (12), where E_c is an energy close to the highest eigenvalue of the system. In other words, instead of calculating $\langle \psi_0 | \psi_n \rangle$ and $\langle \psi_0 | \hat{p} T_n(\hat{H}) \cdot \hat{p} T_m(\hat{H}) | \psi_0 \rangle$, I calculated $\langle \psi_0 | (\hat{H} - E_c)^2 | \psi_n \rangle$ and

$$\langle \psi_0 | (\hat{H} - E_c)^2 \hat{p} T_n(\hat{H}) \cdot \hat{p} T_m(\hat{H}) | \psi_0 \rangle.$$

The corresponding spectra have a factor $(E - E_c)^2$, which needs to be removed. This procedure is useful for the fol-

lowing reasons. In the case of DOS, the factor $(E - E_c)^2$ changes the overwhelming dominance of the higher end of $\rho(E)$, thus avoiding its possible interference to the lower end of the spectrum (which we are interested in) by the tails of the convolution functions. In the case of OAS, the correctness of Eq. (13) depends on $\langle a_i^* a_j \rangle = 0$ for $i \neq j$ of Eq. (6). For the limited number of random wave functions used here, this is not rigorously satisfied. As a result, in Eqs. (12) and (13), a ϕ_i with a high-energy eigenvalue E_i can leave noise to ϕ_i and ϕ_j 's contributions to $\Lambda_{n,m}$, where E_i and E_j are in the lower-energy range. This noise will later show up in the lower-energy region of $\tau(E_1, E_2)$. The factor $(E_i - E_c)^2$ can reduce the magnitude of this noise.

(3) A plane-wave basis is used in the calculation, it produces a more realistic description than a tight-binding basis. The latter is often used with the moments method⁴⁻⁸ and recursion method.^{11,12} Because the full spectrum of a plane-wave Hamiltonian is much broader than a tight-binding spectrum, the interesting region of the spectrum is usually only a small part of the total spectrum. So, a large number of moments is needed to get high resolutions of the spectrum. The largest number of moments I have ever used (for a projected DOS) is 20 000. I saw no numerical instability associated with these large numbers of moments.

(4) I did not use the maximum entropy method^{6,10} in the transformation from moments to energy space functions [Eqs. (4) and (14)]. This is because the nonlinear equations in the maximum entropy method are difficult to solve due to the large number of moments used here, especially for the OAS.

(5) I have shown that a moments method can be used to calculate $\epsilon_2(E)$. It is interesting to compare and connect the moments method with the recursion method.^{8,13} However, the recursion formula is inappropriate for calculating $\epsilon_2(E)$. Also, the behaviors of the recursion method under plane-wave bases are not as well known as those under tight-binding-like bases.

In all the following calculations, I will use empirical pseudopotentials¹⁴ to approximate the single-particle total potential of the system, i.e., $V(\mathbf{r}) = \sum_{\mathbf{R}_a} V_a(|\mathbf{r} - \mathbf{R}_a|)$, where V_a is the empirical potential of atom-type a and \mathbf{R}_a are the positions of the atoms. Si and H atoms are used in the following calculations; their empirical pseudopotentials in the continuous reciprocal space are taken from our recent fit.¹⁵ The wave functions of the system are expanded by a plane-wave basis and an energy cutoff of 4.5 Rv is used in the expansions. A uniform numerical grid of $N_x \times N_y \times N_z$ is used in real space to describe the potential $V(\mathbf{r})$ and the wave function $\psi(\mathbf{r})$. The application of \hat{H} on ψ employs a $N_x \times N_y \times N_z$ FFT to transform ψ from reciprocal space to real space.² In the implementation of Eqs. (4) and (14), I_n and $\Lambda_{n,m}$ have been multiplied by smooth truncation functions, to avoid rapid oscillations of the constructed spectra in E space. Two truncation functions have been used in the calculations: One is $e^{-(n/0.5N_c)^2}$, which corresponds to a Gaussian broadening in energy space; another is $e^{-(n/0.8N_c)^8}$, which corresponds to an oscillatory convolution function

in energy space and will be called ‘‘oscillatory broadening.’’

I first test the current method by comparing the results with those found in *direct* calculations (*direct* means solving all the eigenfunctions of the system). The example used is a 2048 Si-atom supercell. It is generated by applying periodic boundary condition to a supercell which contains $8 \times 8 \times 8 \times 2$ primitive cells of bulk Si. Its eigenstates are identical to those of bulk Si at corresponding *folded* k points. Thus, the eigensolutions can be calculated directly from $\hat{H}\phi_i = E_i\phi_i$. Independently I calculated the results using the current method applied to the 2048 Si-atom supercell. Here, a $64 \times 64 \times 96$ FFT grid is used. As mentioned before, $N_c = 500$ and $N_a = 20$ are used. The computation time for this system is about 3 Cray-YMP CPU hours (only one \hat{p}_k has been calculated).

Figure 1 shows the comparison of the $\rho(E)$ and $\epsilon_2(E)$ between the current method and the direct calculations. Here, the same Gaussian broadening with width of about 0.3 eV is used for both the direct and current method. The spectra agree very well. The static dielectric constant ϵ_1 can be calculated from $\epsilon_2(E)$ according to

$$\epsilon_1 = 1 + \frac{2}{\pi} \int_0^\infty \frac{\epsilon_2(E)}{E} dE . \quad (15)$$

The ϵ_1 's calculated from Fig. 1 are 10.305 and 10.572 for the direct (with broadening) and the current method, respectively. They differ by 2.5%. Using different random wave-function results, I find that the *statistical average error* is about 1.5%, i.e., the same order as the above error. The integral of the $\rho(E)$ up to the gap gives, using the current method, an occupation number of 8162.3e as opposed to the exact occupation number of 8192e. The

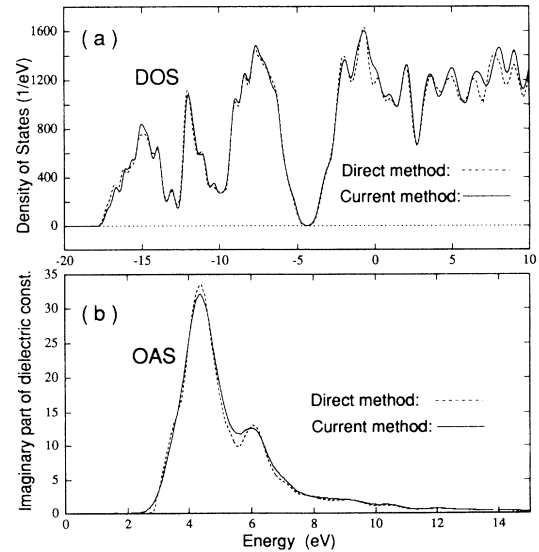


FIG. 1. The spectra of 2048 Si bulk supercell system. The same Gaussian broadening is used in both the current method and direction calculations. (a) Total density of states (only one portion of it is shown; the higher end of the spectra reaches 60 eV); (b) $\epsilon_2(E)$, the imaginary part of the dielectric constant.

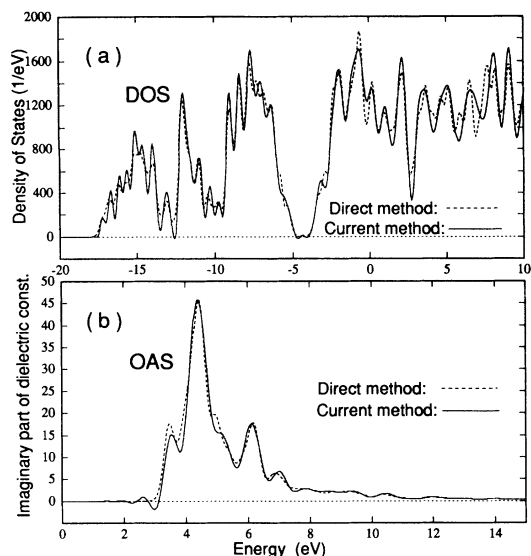


FIG. 2. The spectra of 2048 Si bulk supercell system. The oscillatory broadening is used for the current method, and a 0.1-eV Gaussian broadening is used for the direct calculations. (a) Total density of states; (b) $\epsilon_2(E)$, the imaginary part of the dielectric constant.

error is 0.3%.

In Figure 2, the results of Fig. 1 are shown with different broadening. Here, the oscillatory broadening is used for the current method and a 0.1 eV width Gaussian broadening is used for the direct calculation. The oscillatory broadening gives more detailed structures of the spectra, but tends to over oscillate and even gives negative $\rho(E)$ and $\epsilon_2(E)$ in some regions. The ϵ_1 's calculated from this figure are 10.707 and 10.251 for the direct and current method calculations, respectively. Thus, the error due to the broadening can be 3%. The integration of the $\rho(E)$ up to the gap gives 8161.9e, using the current method, almost the same as the Gaussian broadening result.

I next use the current method to calculate a realistic model of Si quantum dots,^{3,15,16} which cannot be calculated by the conventional direct methods. This system is a quantum box with edges of $23 \times 23 \times 33$ (Å). It contains 1035 Si atoms in a bulk diamond structure and its surface is passivated by 452 H atoms. This system is calculated in a periodic supercell with the quantum dot's surrounding area (60% of the total space) filled by vacuum. The band-edge states of this system have been accurately calculated in previous works.^{3,15} Figure 3 shows its DOS and OAS as calculated by the current method. The DOS band edges match the positions of the exactly calculated^{3,15} band-edge states. The integral of the DOS in Fig. 3 up to the gap gives an occupation number of

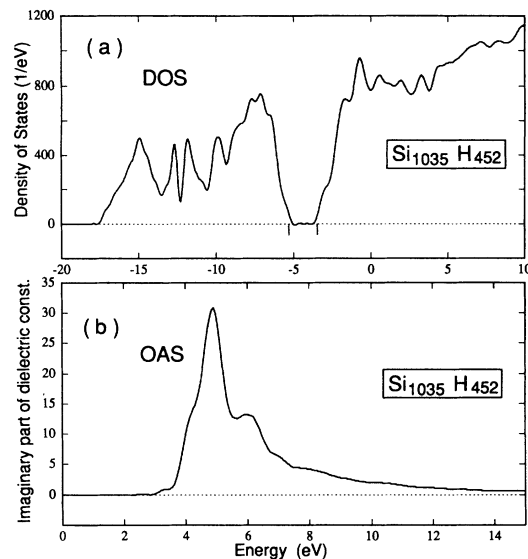


FIG. 3. The spectra of the $\text{Si}_{1035}\text{H}_{452}$ quantum dot. The oscillatory broadening is used for both the DOS and OAS. $N_c = 500$ and $N_a = 20$. It takes 3 Cray-YMP CPU hours. (a) Total density of states (only one portion of it is shown; the higher end of this DOS reaches 60 eV). The short vertical bars are the positions of band-edge states calculated in Refs. 3 and 15. The vacuum level is at 0 eV. Thus, the DOS above 0 eV has contributions for vacuum and should depend on the total volume of vacuum used in the calculation. (b) $\epsilon_2(E)$, the imaginary part of the dielectric constant. Note that $\epsilon_2(E)$ does not depend on the total volume of vacuum used in the calculation.

4566.2e as opposed to the exact number of 4592e. The difference is 0.6%. The ϵ_1 for this quantum box calculated from $\epsilon_2(E)$ is 8.36 and 8.52, for the Gaussian and oscillatory broadening, respectively. Physically, this effective ϵ_1 is defined as $1 + \mathbf{P}/E\mathbf{V}$, here \mathbf{P} is the total polarization of a quantum dot under a constant external electric field \mathbf{E} , and V is the volume of a quantum dot.

In conclusion, I have demonstrated that the moments method can be used with a plane-wave basis to achieve accurate electronic spectra of a thousand-atom system within a few hours of Cray CPU time. In particular, this method can be used to calculate the optical-absorption spectra and the results are good compared with the direct calculations.

I am indebted to S. B. Zhang for drawing my attention to this subject, and to A. Zunger for many discussions and critical reading of the manuscript. This work was supported by the office of Energy Research, Materials Science Division, U. S. Department of Energy, under Grant No. DE-AC02-83CH10093.

¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

²M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

³L. W. Wang and A. Zunger, J. Chem. Phys. **100**, 2394 (1994).

⁴N. I. Akhiezer, *The Classical Moment Problem* (Hafner, New York, 1965).

⁵F. Ducastelle and F. Cyrot-Lackmann, J. Phys. Chem. Solids

- 31, 1295 (1970).
- ⁶I. Turek, J. Phys. C **21**, 3251 (1988).
- ⁷D. A. Drabold and O. F. Sankey, Phys. Rev. Lett. **70**, 3631 (1993).
- ⁸J. C. Wheeler and C. Blumstein, Phys. Rev. B **6**, 4380 (1972); J. C. Wheeler, M. G. Prais, and C. Blumstein, *ibid.* **10**, 2429 (1974).
- ⁹G. Arfken, *Mathematical Methods for Physicists* (Academic, Orlando, 1985).
- ¹⁰J. Skilling, in *Maximum Entropy and Bayesian Methods*, edited by J. Skilling (Kluwer, Dordrecht, Holland, 1983).
- ¹¹See, V. Heine, D. W. Bullett, R. Haydock, and M. J. Kelley, *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.
- ¹²P. G. Pettifor and D. L. Weaire, *The Recursion Method and Its Applications* (Springer-Verlag, Berlin, 1984).
- ¹³P. Lambin and J-P. Gaspard, Phys. Rev. B **26**, 4356 (1982).
- ¹⁴M. L. Cohen and J. R. Chelikowsky, *Electronic Structure and Optical Properties of Semiconductors* (Springer-Verlag, Berlin, 1988).
- ¹⁵L. W. Wang and A. Zunger, J. Phys. Chem. (to be published).
- ¹⁶M. G. Bawendi, M. L. Stiegerwal, and L. E. Brus, Ann. Phys. Phys. Chem. **41**, 477 (1990).