Green's-function approach to quantum confinement

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We present a rigorous means of computing the electronic properties of a confined system by perturbing the electronic properties of an unconfined, bulk system. Our approach focuses on the Green's function of the confined system. We explain why it is preferable to consider the confined Green's function rather than the confined energy eigenfunctions, and an expression for the change in the Green's function produced by quantum confinement is derived. Finally, we shift our focus to the eigenfunctions and derive approximate results for a spherical nanocrystal with a Green's function methodology. [S0163-1829(98)01515-X]

I. INTRODUCTION

It makes intuitive sense that the physical properties of a sufficiently large, confined system should be similar to the physical properties of the corresponding unconfined, bulk system. However, it is not apparent how to express this similarity quantitatively. The eigenfunctions of the two systems are qualitatively different: the eigenfunctions of a confined system are standing waves, while the natural eigenfunctions of a bulk crystal, calculated using translational symmetries, are running Bloch waves. Nevertheless, the measureable properties of the two systems must be related. In this paper, we present a formal description of quantum confinement physics that clarifies this relationship. We treat the confining surface as a source of translational symmetry breaking. Our analysis provides a quantitative description of how translational symmetry breaking perturbs the properties of the bulk.

This treatment relies on the use of Green's functions. In Sec. II, we explain why it is preferable to focus on Green's functions rather than energy eigenfunctions when exploring the physical consequences of broken symmetry. In Sec. III, we show how to express the Green's function of a confined system as the Green's function of the bulk system plus a perturbation. A series expansion for the perturbation is derived in Sec. IV. We consider the impact of translational symmetry breaking on the measureable properties of the confined system in Sec. V. In Sec. VI, we shift our attention from the Green's function of the confined system to the confined wave functions, and we compute approximate eigenenergies and eigenfunctions for a spherical nanocrystal.

II. BROKEN SYMMETRY AND GREEN'S FUNCTIONS

In quantum mechanics, symmetries in the Hamiltonian lead to degeneracies in the energy eigenfunctions. Degenerate eigenfunctions can be arbitrarily superposed without jeopardizing their status as eigenfunctions. Thus, in situations of high symmetry, there is a lot of flexibility in choosing how to express the eigenfunctions. When we introduce a small perturbation into a highly symmetric situation, typically degeneracy is lifted, and the flexibility is lost. A major redefinition of the eigenfunctions can result from the perturbation, as is described by degenerate perturbation theory.

Although this major redefinition can occur, if the perturbation is small the physical properties of the system generally should only change slightly. This fact is physically obvious, but it is obscured if we pay excessive attention to the energy eigenfunctions. It is therefore useful to work with a quantity characterizing a system that does not suffer such a radical transformation under a small perturbation. One such quantity is the Green's function. If the eigenfunctions of a system are $\psi_n(\vec{r})$ and the eigenenergies are E_n, the Green's function is defined by

$$\mathcal{G}(\vec{r},\vec{r}',E) = \Sigma_n \psi_n(\vec{r}) \psi_n^*(\vec{r}') \left[\frac{\Theta(E_F - E_n)}{E - E_n - i\eta} + \frac{\Theta(E_n - E_F)}{E - E_n + i\eta} \right],$$
(1)

where, throughout this paper, η is an infinitesimal positive quantity. In this equation, E_F denotes the Fermi energy and Θ is the Heaviside function. The infinitesimal imaginary terms in the factor in brackets appear in such a way as to agree with the definition of the single-particle Green's function in many-body theory.[1] It is clear from expression (1) that the Green's function is unaltered by a mere redefinition of the degenerate states of a given energy. On physical grounds, it is reasonable that the Green's function should be unaltered by an inessential redefinition because the time-dependent Green's function is the propagator that advances states in time.[2]

The Dyson equation[1] specifies how an unperturbed Green's function $\mathcal{G}_u$ is perturbed to $\mathcal{G}_p$ under a potential $V(\vec{r})$:

$$\mathcal{G}_p(\vec{r},\vec{r}',E) = \mathcal{G}_u(\vec{r},\vec{r}',E)$$
$$+ \int d^3\vec{r}'' \mathcal{G}_u(\vec{r},\vec{r}'',E) V(\vec{r}'') \mathcal{G}_p(\vec{r}'',\vec{r}',E). \quad (2)$$

No separate degenerate perturbation theory is required for the Green's function as is required for the energy eigenfunctions. This is because of the insensitivity of the Green's function to the redefinition of degenerate states: the Green's function changes in a tidy way under a perturbation, regardless of how much degeneracy exists in the unperturbed system. As a

result of this tidiness, the Green's function is an ideal quantity for describing many physical effects of a symmetry breaking perturbation.

III. BROKEN TRANSLATIONAL SYMMETRY AND GREEN'S FUNCTIONS

In the case of quantum confinement, the translational symmetry of the system is broken by the presence of a surface. Degenerate Bloch eigenfunctions of the unconfined, bulk system are superposed into qualitatively different standing wave eigenfunctions. To clarify the relationship between the physical properties of a confined system and the physical properties of an unconfined system, we ignore the radical change in the wave functions and focus instead on the Green's function. This was the direction taken by Peierls, who employed the Green's function to justify the use of periodic boundary conditions.[3]

Let us refer to the Green's function of an unconfined, bulk system as $\mathcal{G}_b$. To describe the condition of confinement, it is natural to look for some perturbation potential, V, that breaks translational symmetry. The potential would determine the confined Green's function from the unconfined Green's function through the Dyson equation. Unfortunately, such an approach proves to be problematic. The confined system's potential and the unconfined system's potential differ everywhere outside the confined system; the integral in the Dyson equation diverges.

It turns out to be more fruitful to take another tact by pursuing a boundary value approach, adapting the work on electromagnetic waves in a cavity of Ref. 4. To describe this approach, we first consider the case of bulk electrons. The electronic eigenfunctions of a bulk system satisfy the effective one-particle Schrödinger equation

$$H_b \psi(\vec{r}) = [-\nabla^2 + V_b(\vec{r})] \psi(\vec{r}) = E \psi(\vec{r}), \qquad (3)$$

with periodic boundary conditions. Here, we adopt atomic units. The solution to this equation can be obtained by exploiting the translational symmetries of the bulk system. The eigenfunctions take the form of Bloch waves, $\psi_{n,\vec{k}}$, labeled by a band index n and a crystal momentum $\vec{k}$. The eigenenergies are given by a band-structure function $E_n(\vec{k})$. In the bulk crystal, electrons occupy eigenstates up to a Fermi energy E_F. The energy-dependent bulk Green's function satisfies the equation

$$(H_b - E)\mathcal{G}_b(\vec{r}, \vec{r}', E) = -\delta(\vec{r} - \vec{r}'). \qquad (4)$$

In terms of the Bloch eigenfunctions of the system, the Green's function takes the form

$$\mathcal{G}_b(\vec{r}, \vec{r}', E) = \Sigma_{n,\vec{k}} \psi_{n,\vec{k}}(\vec{r}) \psi_{n,\vec{k}}^*(\vec{r}') \left[\frac{\Theta(E_F - E_n(\vec{k}))}{E - E_n(\vec{k}) - i\eta} \right.$$

$$\left. + \frac{\Theta(E_n(\vec{k}) - E_F)}{E - E_n(\vec{k}) + i\eta} \right]. \qquad (5)$$

To describe the Green's function of a confined system, we assume that the Hamiltonian in the interior of the confined system is similar to that of the bulk system. Thus, for $\vec{r}$

inside the confined system, the confined Green's function, $\mathcal{G}_c(\vec{r}, \vec{r}', E)$, should satisfy Eq. (4) just as the bulk Green's function does. To describe the condition of confinement, we simply impose boundary conditions on the confined Green's function at the surface. Let us express the confined Green's function as the bulk Green's function plus a confinement perturbation

$$\mathcal{G}_c(\vec{r}, \vec{r}', E) = \mathcal{G}_b(\vec{r}, \vec{r}', E) + \Delta \mathcal{G}(\vec{r}, \vec{r}', E). \qquad (6)$$

Since both $\mathcal{G}_b$ and $\mathcal{G}_c$ satisfy Eq. (4), the perturbation obeys the homogeneous equation

$$(H_b - E)\Delta \mathcal{G}(\vec{r}, \vec{r}', E) = 0. \qquad (7)$$

If we demand that the confined Green's function vanish at the surface, Eq. (6) requires that

$$\Delta \mathcal{G}(\vec{r}_s, \vec{r}', E) = -\mathcal{G}_b(\vec{r}_s, \vec{r}', E) \qquad (8)$$

for surface points $\vec{r}_s$. We have shown that translational symmetry breaking changes the Green's function by a perturbation. The perturbation satisfies differential Eq. (7) with boundary condition (8). Now our task is to solve this equation.

Before undertaking this problem, we point out that the boundary condition (8) captures the essential physics of confinement. However, it is possible to extend the formalism to include more subtle effects such as charge redistribution at the surface of a confined system. This can be achieved by perturbing the many-body Green's function $i\mathcal{G}_b(\vec{r}, t, \vec{r}', t') \equiv \langle \Psi_b | T\{\psi(\vec{r}, t)\psi(\vec{r}', t')\} | \Psi_b \rangle$ and using the fact that it satisfies the differential equation[1]

$$\left(E + \nabla^2 - U_b(\vec{r}) \right) \mathcal{G}_b(\vec{r}, \vec{r}', E)$$

$$= \delta(\vec{r} - \vec{r}') + \int d^3 r'' \Sigma^*(\vec{r}, \vec{r}'', E; \mathcal{G}_b) \mathcal{G}_b(\vec{r}'', \vec{r}', E). \qquad (9)$$

IV. FORMAL SOLUTION FOR CONFINEMENT GREEN'S FUNCTION

We derive a solution to Eq. (7) by continuing to adapt the work of Ref. 4. We write the perturbation $\Delta \mathcal{G}$ in the form of a layer potential

$$\Delta \mathcal{G}(\vec{r}, \vec{r}', E) = \int d^2 \vec{\alpha} \frac{\partial}{\partial n_\alpha} \mathcal{G}_b(\vec{r}, \vec{\alpha}, E) \mu(\vec{\alpha}, \vec{r}', E) \qquad (10)$$

where $\mu(\vec{\alpha}, \vec{r}', E)$ is an unknown source density. In this two-dimensional integral, $\vec{\alpha}$ is a vector that ranges over all points on the surface, and n_α denotes the normal to the surface at $\vec{\alpha}$. Written in this integral form, $\Delta \mathcal{G}(\vec{r}, \vec{r}', E)$ will satisfy Eq. (7) for $\vec{r}$ inside the surface, regardless of μ.[5]

We therefore need only impose the boundary condition (8). We require that

$$\lim_{\vec{r}\to\vec{r}_s}\int d^2\vec{\alpha}\frac{\partial}{\partial n_\alpha}\mathcal{G}_b(\vec{r},\vec{\alpha},E)\mu(\vec{\alpha},\vec{r}',E)=-\mathcal{G}_b(\vec{r}_s,\vec{r}',E),$$

(11)

where $\vec{r}_s$ is a point on the surface. We cannot simply set $\vec{r}$ equal to $\vec{r}_s$ in the integral on the left hand side of this equation, because $\mathcal{G}_b(\vec{r}_s,\vec{\alpha},E)$ is poorly behaved as $\vec{\alpha}\to\vec{r}_s$. To evaluate the limit, we first show that

$$\mathcal{G}_b(\vec{r},\vec{r}',E)=-\frac{1}{4\pi|\vec{r}-\vec{r}'|}+\mathcal{H}(\vec{r},\vec{r}',E),$$

(12)

where $\mathcal{H}(\vec{r},\vec{r}',E)$ is finite at $\vec{r}=\vec{r}'$.

We begin with the differential Eq. (4). Writing $\mathcal{G}_b$ in the form (12), it follows that $\mathcal{H}$ satisfies the equation

$$(H_b-E)\mathcal{H}(\vec{r},\vec{r}',E)=[V_b(\vec{r})-E]\frac{1}{4\pi|\vec{r}-\vec{r}'|}.$$

(13)

Using the definition (5) of the Green's function, we can write $\mathcal{H}$ in the form

$$\mathcal{H}(\vec{r},\vec{r}',E)=-\int d\vec{r}''\mathcal{G}_b(\vec{r},\vec{r}'',E)[V_b(\vec{r}'')-E]\frac{1}{4\pi|\vec{r}''-\vec{r}'|}$$

(14)

$$=\int d\vec{r}''\frac{1}{4\pi|\vec{r}-\vec{r}''|}[V_b(\vec{r}'')-E]\frac{1}{4\pi|\vec{r}''-\vec{r}'|}$$

$$-\int d\vec{r}''\mathcal{H}(\vec{r},\vec{r}'',E)[V_b(\vec{r}'')-E]\frac{1}{4\pi|\vec{r}''-\vec{r}'|}$$

$$\equiv\mathcal{I}(\vec{r},\vec{r}',E)+\mathcal{J}(\vec{r},\vec{r}',E).$$

By inspecting its definition, we can confirm that $\mathcal{I}(\vec{r},\vec{r}',E)$ is finite at $\vec{r}=\vec{r}'$. To show that $\mathcal{J}(\vec{r},\vec{r}',E)$ is also well behaved at $\vec{r}=\vec{r}'$, we note that it satisfies the differential equation

$$(H_b-E)\mathcal{J}(\vec{r},\vec{r}',E)=-[V_b(\vec{r})-E]\mathcal{I}(\vec{r},\vec{r}',E).$$

(15)

Since $\mathcal{I}$ is finite at $\vec{r}=\vec{r}'$, generically $\mathcal{J}$ should be too. Thus, $\mathcal{H}=\mathcal{I}+\mathcal{J}$ should be well behaved at $\vec{r}=\vec{r}'$, as asserted.

Now that we have characterized the singularity in $\mathcal{G}_b$, we appeal to the identity[5]

$$\lim_{z\to0^-}\frac{\partial}{\partial z}\frac{-1}{4\pi\sqrt{(x^2+y^2+z^2)}}=-\frac{1}{2}\delta(x)\delta(y).$$

(16)

From this identity and from Eq. (12), it follows that limit (11) is

$$-\frac{1}{2}\mu(\vec{r}_s,\vec{r}',E)+\int d^2\vec{\alpha}\frac{\partial}{\partial n_\alpha}\mathcal{G}_b(\vec{r}_s,\vec{\alpha},E)\mu(\vec{\alpha},\vec{r}',E)$$

$$=-\mathcal{G}_b(\vec{r}_s,\vec{r}',E)$$

(17)

where the first term on the left hand side arises because of the δ function. This is a "Dyson" type equation for μ,

which provides a formal solution for $\Delta\mathcal{G}$ via Eq. (10). Iterating Eq. (17), and recalling definition (6), we find that

$$\Delta\mathcal{G}(\vec{r},\vec{r}',E)=2\int d^2\vec{\alpha}\frac{\partial\mathcal{G}_b(\vec{r},\vec{\alpha},E)}{\partial n_\alpha}\mathcal{G}_b(\vec{\alpha},\vec{r}',E)$$

$$+2^2\int d^2\vec{\alpha}d^2\vec{\beta}\frac{\partial\mathcal{G}_b(\vec{r},\vec{\alpha},E)}{\partial n_\alpha}\frac{\partial\mathcal{G}_b(\vec{\alpha},\vec{\beta},E)}{\partial n_\beta}$$

$$\times\mathcal{G}_b(\vec{\beta},\vec{r}',E)$$

$$+\cdots.$$

(18)

This is a formal expression for the change in the Green's function arising from translational symmetry breaking. It may be regarded as analogous to the usual iterated Dyson equation, but with an "electron-boundary" interaction occurring only at the surface.

V. PHYSICAL EFFECTS OF TRANSLATIONAL SYMMETRY BREAKING

Using $\Delta\mathcal{G}$, any electronic property that is expressable in terms of the Green's function can be written for the confined system as the corresponding bulk property plus a perturbation. We illustrate this with two examples.

The charge density in a confined structure is given by[1]

$$\rho_c(\vec{r})=2\int\frac{dE}{2\pi i}e^{iE\eta}\mathcal{G}_c(\vec{r},\vec{r},E).$$

(19)

Using Eq. (6), we can write this as

$$\rho_c(\vec{r})=2\int\frac{dE}{2\pi i}e^{iE\eta}[\mathcal{G}_b(\vec{r},\vec{r},E)+\Delta\mathcal{G}(\vec{r},\vec{r},E)]$$

$$=\rho_b(\vec{r})+\Delta\rho(\vec{r}).$$

(20)

On physical grounds, we expect that $\Delta\rho(\vec{r})$ should be small deep inside a confined system and should grow in magnitude near the surface.

For optical properties, the imaginary part of the dielectric constant is a quantity of interest. In terms of energy eigenfunctions, it is given by[6]

$$\epsilon_c^{(2)}(\omega)=\left(\frac{2\pi e}{m\omega}\right)^2\frac{1}{V}\Sigma_{f,i}|\langle f|\hat{\varepsilon}\cdot\vec{p}|i\rangle|^2\delta(E_f-E_i-\omega),$$

(21)

where f denotes a final confined eigenfunction, i denotes an initial confined eigenfunction, $\hat{\varepsilon}$ is a photon polarization vector, and $\vec{p}$ is the momentum operator, and V is the nanocrystal volume. In terms of the Green's function, we can write $\epsilon_c^{(2)}(\omega)$ in the form

$$\epsilon_c^{(2)}(\omega)=\text{Re}\left[\left(\frac{c}{\omega}\right)^2\frac{1}{V}\int d^3\vec{r}d^3\vec{r}'dE_idE_f\hat{\varepsilon}\cdot\vec{p}\mathcal{G}_c(\vec{r},\vec{r}',E_i)\right.$$

$$\left.\times\hat{\varepsilon}\cdot\vec{p}'\mathcal{G}_c(\vec{r},\vec{r}',E_f)\delta(E_f-E_i-\omega)\right].$$

(22)

Here, $\vec{p}'$ is a momentum operator that differentiates with respect to $\vec{r}'$. The spatial integrals proceed over the interior of the confined system only. Using Eqs. (6) and (22), it is straightforward to arrive at an expression of the form

$$\epsilon_c^{(2)}(\omega) = \epsilon_b^{(2)}(\omega) + \Delta\epsilon^{(2)}(\omega), \qquad (23)$$

where $\epsilon_b^{(2)}$ is the bulk function and $\Delta\epsilon^{(2)}$ gives the change due to confinement effects. In a semiconductor nanocrystal, for instance, we expect the term $\Delta\epsilon^{(2)}(\omega)$ to be negative just above the energy of the bulk gap. This will suppress absorption and increase the size of the gap, which is a typical quantum confinement effect.

VI. CONFINED WAVE FUNCTIONS AND EIGENENERGIES

So far in this paper, we have stressed the utility of the Green's function over the eigenfunctions in describing the effects of quantum confinement. There are instances, however, in which it is desirable to determine the eigenfunctions of a confined structure. Even for this purpose, a Green's function approach is of use. The wave functions of a confined structure can be regarded as a superposition of bulk Bloch eigenfunctions that cancel at the surface. In previous papers, we have successfully constructed this superposition by first forming a basis of Wannier functions.[7] Here, we determine the proper superposition of Bloch eigenfunctions using the bulk Green's function.

The electronic wave functions of the confined system satisfy Eq. (3) with the requirement that ψ vanish on the surface. We multiply Eq. (3) by $\mathcal{G}_b$, multiply Eq. (4) by ψ, and then subtract. Integrating the difference over the interior of the confined system, we obtain

$$\psi(\vec{r}) = \int [\psi(\vec{r}')\nabla^2\mathcal{G}_b(\vec{r},\vec{r}',E) - \mathcal{G}_b(\vec{r},\vec{r}',E)\nabla^2\psi(\vec{r}')]d^3\vec{r}', \qquad (24)$$

where $\vec{r}$ is a point in the interior of the confined system. Using the divergence theorem, and the fact that ψ must vanish on the surface of the confined system, we arrive at

$$\psi(\vec{r}) = -\int \mathcal{G}_b(\vec{r},\vec{r}',E)\frac{\partial\psi}{\partial n'}d^2\vec{r}' = \int \mathcal{G}_b(\vec{r},\vec{r}',E)\mu(\vec{r}')d^2\vec{r}', \qquad (25)$$

where the integral is taken over the surface. In this equation, the factor $\mu(\vec{r}')$ should be regarded as an unknown surface density producing the wave function on the interior. For only special values of E—the eigenenergies of the confined system—is it possible to find a nonzero μ that gives rise to a nonzero wave function ψ that manages to vanish on the surface. At these special values of E, once the proper μ has been found, Eq. (25) gives the eigenfunction ψ.

It appears from Eq. (5) that $\mathcal{G}_b(\vec{r},\vec{r}',E)$ depends upon eigenstates with all energies. However, for a bulk system, the sum over $\vec{k}$ states in the equation can be turned into an integral over energies and an integral over states of constant energy. If E is among the eigenenergies of H_b, then the integrand has poles at $E_n(\vec{k}) = E \pm i\eta$. The integral over energies can then be contracted to integrals around $E \pm \eta$ in the complex plane. Hence, despite appearances, the $\mathcal{G}_b(\vec{r},\vec{r}',E)$ involves only states of energy E. Thus, the integral (25) is really just a way of expressing ψ as a superposition of bulk states of energy E.

Equation (25) gives an efficient way to determine the eigenstates of a confined system because it is a two-dimensional integral equation that replaces the usual three-dimensional Schrodinger equation in three dimensions. A numerical solution of Eq. (25) is currently being pursued for real systems. However, it is also possible to derive an approximate solution to Eq. (25) analytically for a spherical nanocrystal.

We begin by computing an approximation to the bulk Green's function (5). Let us write the Bloch waves in Eq. (5) as a superposition of localized Wannier functions:[8]

$$\mathcal{G}_b(\vec{r},\vec{r}',E) = \frac{1}{N}\Sigma_{n,\vec{k}}\Sigma_{\vec{R}}e^{i\vec{k}\cdot\vec{R}}a_n(\vec{r}-\vec{R})\Sigma_{\vec{R}'}e^{-i\vec{k}\cdot\vec{R}'}a_n^*(\vec{r}'-\vec{R}')\left[\frac{\Theta(E_F-E_n(\vec{k}))}{E-E_n(\vec{k})-i\eta} + \frac{\Theta(E_n(\vec{k})-E_F)}{E-E_n(\vec{k})+i\eta}\right]$$

$$= \frac{V}{N}\Sigma_{n,\vec{R},\vec{R}'}a_n(\vec{r}-\vec{R})a_n^*(\vec{r}-\vec{R}')\int_{BZ}\frac{d^3k}{(2\pi)^3}e^{i\vec{k}\cdot(\vec{R}-\vec{R}')}\left[\frac{\Theta(E_F-E_n(\vec{k}))}{E-E_n(\vec{k})-i\eta} + \frac{\Theta(E_n(\vec{k})-E_F)}{E-E_n(\vec{k})+i\eta}\right]$$

$$\approx \int_{BZ}\frac{d^3k}{(2\pi)^3}e^{i\vec{k}\cdot(\vec{r}-\vec{r}')}\left[\frac{\Theta(E_F-E_n(|\vec{k}|))}{E-E_n(|\vec{k}|)-i\eta} + \frac{\Theta(E_n(|\vec{k}|)-E_F)}{E-E_n(|\vec{k}|)+i\eta}\right]$$

$$\approx \left[\left(\frac{2k}{dE_n(k)/dk}\right) - \left(\frac{e^{-ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}\Theta(E_F-E) - \frac{e^{ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}\Theta(E-E_F)\right)\right]_{E_n(k)=E}. \qquad (26)$$

In this equation, N refers to the number of unit cells in the bulk crystal and V refers to the volume of the bulk crystal. In the third line, the Wannier functions are assumed to be perfectly localized. The bands are also assumed to be spherically symmetrical, so that $E_n(\vec{k}) = E_n(|\vec{k}|)$. In the final line, it is assumed that the surface $E = E_n(|\vec{k}|)$ is a sphere in the Brillouin zone satisfied by a single band only. We can now insert our expression for $\mathcal{G}_b$ into Eq. (25). The resulting integral equation for ψ is actually closely related to the differential equation obtained in the effective mass approximation.[9] In both cases, one assumes that the Wannier functions are localized and solves for what turns out to be a sort of envelope function.

With our approximation for $\mathcal{G}_b$, the solution to Eq. (25) can be found by inspection for a spherical nanocrystal. For each band n, we guess that μ can take the form

$$\mu(\vec{r}') = Y_{l,m}(\hat{r}') \qquad (27)$$

for any choice of l and m. The corresponding wave function is found to involve spherical Bessel functions: $\psi(\vec{r}) \sim j_l(k_l r) Y_{l,m}(\hat{r})$. If the value of k_l satisfies $j_l(k_l a) = 0$, where a is the radius of the nanocrystal, then ψ vanishes at the nanocrystal surface as required. The energy of ψ is $E_n(|\vec{k}| = k_l)$, where, as we recall, all bands have been assumed to be spherically symmetrical.

In particular, the highest occupied electronic state and the lowest unoccupied electronic state are found to be proportional to $j_0[(\pi/a)r]$. The energies of these states are therefore $E_v(|\vec{k}| = \pi/a)$ and $E_c(|\vec{k}| = \pi/a)$, respectively, where v refers to the valence band of the bulk and c refers to the conduction band. The resulting energy gap $E_g(a) = E_c(|\vec{k}| = \pi/a) - E_v(|\vec{k}| = \pi/a)$ is plotted versus a in Fig. 1 for InAs nanocrystals. In this plot, we took the spherically symmetrized band function $E_n(|\vec{k}|)$ to be the actual band function $E_n(\vec{k})$ evaluated a distance $|\vec{k}|$ along the X direction. Then, we repeated the calculation choosing the L direction instead. Both calculations are shown, with a comparison to an effective mass computation[9] and to experimental data.[10] Our calculations are in better agreement with experiment than the effective mass treatment. This is because we assume that the bands are independent of the direction of $\vec{k}$, but we make no assumptions as to their dependence on the magnitude of $\vec{k}$. In the effective mass calculation, one assumes that the bands are not only spherically symmetric but also parabolic.

VII. CONCLUSION

We have drawn a quantitative connection between the Green's function of a confined system, like a nanocrystal,
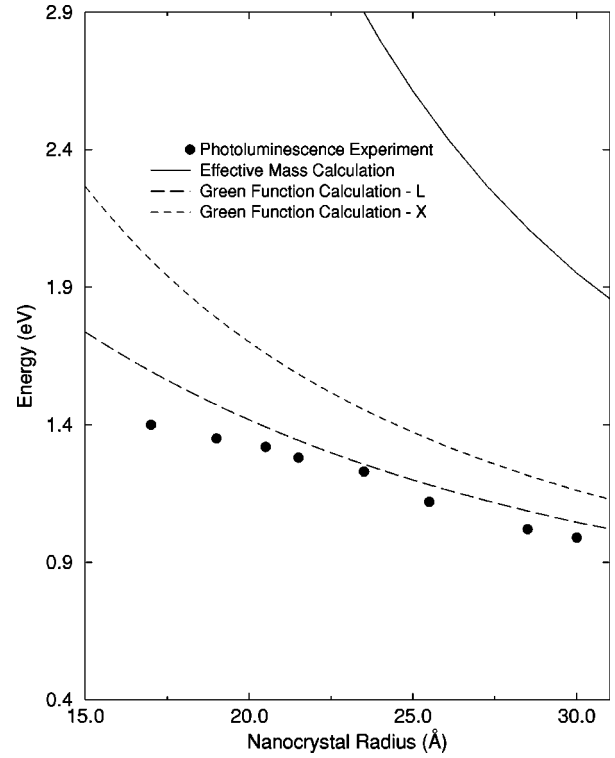

FIG. 1. Energy gaps of InAs nanocrystals. Green's function calculations show better agreement with experiment than effective mass calculation. See text for explanation of difference between two Green's function calculations.

and the Green's function of a bulk system. We presented a formal expression for the perturbation in the Green's function due to quantum confinement effects, and then considered the measureable consequences of this perturbation. An approximate expression for the confined eigenfunctions and eigenenergies was derived as well. Applications of this formalism to real systems are in progress. The development presented here could find use in the study of confined phonons and photons as well as electrons.

ACKNOWLEDGMENTS

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