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Calculation of the line shapes of electronic transitions at defects using the frozen Gaussian technique

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Abstract

Calculations of the optical properties of defects in semiconductors or multiphonon transition rates presently make far more severe approximations than standard electronic structure calculations. One major challenge is how one can handle realistically the lattice vibrations, including quantum nuclear dynamics when those are necessary. The semi-classical frozen Gaussian technique allows us to calculate the line shapes of electronic transitions at defects using molecular dynamic simulation data from the initial and final states. Approximate nuclear wave functions are constructed from classical trajectories on nuclear potential energy surfaces for the two states. The method expands the system initial and final states (functions of position and momentum), as a sum of Gaussians, whose centres evolve classically on the relevant potential surface. An expression for the transition probability is then derived from the time-dependent overlap of the two wave functions. The frozen Gaussian method has been tested on the core exciton in diamond. The potential energy surfaces are calculated using an approximate but self-consistent molecular orbital technique, while simultaneously performing molecular dynamics. The results of our calculations show a Stokes shift of 3.64 eV, similar to the value of "up to 5 eV" obtained experimentally. We predict a fine structure with much narrower lines than those observable in the (low-resolution) experimental spectra.

Keywords: Transitions; Line shapes; Defects; Diamond; Core exciton

1. Introduction

The advances made in computational modelling of condensed matter systems in the last decade make it possible to predict many quantities, such as electronic energy levels, wave functions, charge densities and vibrational modes of defects in crystals, reliably and accurately. Yet, while there is much experimental data available for optical line shapes and non-radiative transitions, it can only currently be compared with the most approximate theoretical models (typically single-frequency models or weak coupling models). For these line shapes and rates, a key quantity is the line-shape function.

Here, a new method is proposed to calculate the line-shape function, namely the frozen Gaussian approximation [1,2]. The approach does not make the usual analysis of the motion into normal modes, and can exploit the more flexible tool of molecular dynamics. The frozen Gaussian approximation (FGA) is a mathematical device whereby an approximate nuclear wave function is constructed from ensembles of classical nuclear trajectories on excited and ground state electronic potential energy surfaces (PES). The line-shape function is given by the Fourier transform of the time-dependent overlap of the excited and ground state phonon wave functions. The method is described in detail in Section 2. The principal advantage of the method over previous techniques is that it is not limited to a harmonic description of the nuclear motion, nor to one or just a few phonon modes. The problems encountered when applying this technique are discussed in Section 3, and a simple illustration of the method shown in Section 4.

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2. The calculation of transition rates

A transition between two states can be described to first order in time-dependent perturbation theory, using Fermi's Golden Rule. The initial and final states of the system, Ψ_i and Ψ_f (with energies E_i and E_f, respectively), are assumed to be eigenstates of the system Hamiltonian H_0. The transition is driven by the perturbation H_I which can impart energy E to the system. The resultant expression for the transition rate is

$$W_{if} = \frac{2\pi}{\hbar}|\langle\Psi_i|H_I|\Psi_f\rangle|^2\delta(E_f - E_i - E). \quad (1)$$

In the Born Oppenheimer approximation, the eigenstates of H_0, $\Psi_{i\mu}$ are separated into products of electronic states ψ_i and phonon states $\chi_{i\mu}$, where the electronic states are eigenstates of the Hamiltonian for a given instantaneous nuclear configuration and the phonon states are eigenstates of the nuclear kinetic energy operator and the potential field provided by the electrons. To evaluate the transition between electronic levels i and f it is therefore necessary to average over the initial distribution of phonon states and sum over all final phonon states, arriving at the following expression for the rate:

$$W_{if} = \frac{2\pi}{\hbar}\sum_{\mu\nu}\frac{e^{-\beta E_{i\mu}}}{Z} \times|\langle\psi_i\chi_{i\mu}|H_I|\psi_f\chi_{fv}\rangle|^2\delta(E_{fv} - E_{i\mu} - E), \quad (2)$$

where

$$Z = \sum_{\mu} e^{-\beta E_{i\mu}}.$$

For allowed optical transitions, we make the standard Condon approximation that the transition operator H_I is independent of the nuclear configuration [3]. Eq. (2) is then simplified by replacing the delta function by its Fourier transform, expressing the phonon state χ_μ at time t propagated on potential energy surface i as $e^{-iH_i t/\hbar}|\chi_\mu(0)\rangle = |\chi_\mu(t)\rangle_i$, and replacing the complete sum over final phonon states by unity. Hence the transition rate reduces to thermal average of the Fourier transform of the overlap of the phonon state χ_μ propagated on the initial, i, and final, f, potential energy surfaces:

$$W_{if}(E) = \frac{|\langle\psi_f|H_I|\psi_i\rangle|^2}{\hbar^2} \times\sum_{\mu}\frac{e^{-\beta E_{i\mu}}}{Z}\int_{-\infty}^{\infty} dt\, e_f^{iEt/\hbar}\langle\chi_\mu(t)|\chi_\mu(t)\rangle_i. \quad (3)$$

Eq. (3) is still difficult to evaluate because it depends upon the phonon state as a function of time. The frozen Gaussian approach can be used to construct an approximate nuclear wave function rendering the above expression tractable. The mathematical derivation of the method is given elsewhere [4–8], but the essentials for its use on condensed matter systems follow.

The initial state of the system is approximated by a product of Gaussians, each one describing one of the $3N$ coordinates of the system, whether normal modes or components of individual atomic displacements.

$$\chi(0, R) = \prod_j^{3N}\left(\frac{2\gamma}{\pi}\right)^{1/4}\exp(-\gamma(R - R_j)^2 + iP_j(R - R_j)), \quad (4)$$

where R_j and P_j are the initial positions and momenta of the atoms (or normal mode coordinates). The product is over the $3N$ atom coordinates (or normal modes) of a system containing N atoms, and γ is the Gaussian width, which will be discussed later. Then it can be shown that at later times, t, the nuclear wave function becomes:

$$\chi(t, R) = \exp(iS(t)/\hbar)\prod_j^{3N}\left(\frac{2\gamma}{\pi}\right)^{1/4} \times\exp(-\gamma(R - R_j(t))^2 + iP_j(t)(R - R_j(t))), \quad (5)$$

where $S(t) = \int_0^t L\, dt$, where L closely related to the Lagrangian of the system: $L = KE - PE + \text{zero}$ point energy for the oscillators. The expressions for the absorption and emission spectra for the transition are proportional to the line-shape function $G_{if}(E)$ [3]:

$$G_{if}(E) = \sum_{\mu}\frac{\exp(-\beta E_{i\mu})}{Z}\int_{-\infty}^{\infty} dt\, e_f^{iEt/\hbar}\langle\chi_\mu(t)|\chi_\mu(t)\rangle_i. \quad (6)$$

The sum is over all possible starting configurations, μ. The sum is approximated by selecting a number of starting configurations with random displacements of the atoms about their initial state equilibrium positions.

This treatment has made a number of assumptions, which have been explored in more detail elsewhere [4–10]:

1. The expansion of each degree of freedom in the exact wave function into an overcomplete set of Gaussians is replaced by a single Gaussian per degree of freedom [7,8,10].
2. The nuclear overlap is independent of the Gaussian's width, γ [9]. There proves to be a weak dependence, because of the finite number of starting configurations, but the results are largely independent of γ.
3. A complex function of the momenta and positions of the atoms (or normal modes) ($C(R_i, P_i, t)$ of Ref. [9]) arising in the exact propagation of the Gaussians has been approximated by a constant. This is examined and partially justified in Refs. [2,7,10].

To summarise, one must calculate the positions and momenta of the atoms near the excitation position, both in the excited state of the transition and in its ground state, as functions of time. For each pair of dynamic runs, which start with the same initial positions, the overlap between the Gaussians is calculated as a function of time. For finite temperatures, either the normal mode phonons of the atoms concerned are excited, or sufficient different random displacements of the atoms around their equilibrium positions are included. The number of dynamic runs required before the line-shape function converges depends upon the system. In this case less than ten runs were required.

3. Using the frozen Gaussian method

In the past, the frozen Gaussian method has only been used for a very limited set of systems, but it has huge potential in the field of condensed matter physics. Much information on the structure and properties of defects is contained in the vibronic line shapes of their transitions, and they have only been interpreted by simple weak-coupling or single-frequency models.

Blake and Metiu [8] have studied the absorption lineshape for electrons solvated in halo-sodalites. A mixture of the more sophisticated Herman and Kluk approach [2] and the original frozen Gaussian method [1] has been implemented by Ovchinnikov and Apkarian [10] to study Cl_2 in solid Ar clusters.

The implementation of the method has the following requirements:

- A number of long dynamic runs (of the order of picoseconds) is required to obtain sufficient resolution in the spectra,
- short time steps must be used in the dynamics, to obtain sufficient accuracy in the numerical integration of the action, S,
- reasonably accurate electronic and vibrational states must be modelled,
- the ground state and the excited state must be modelled simultaneously,
- neither calculation must diverge (many methods that force convergence also damp the nuclear motion, and this would not be acceptable).

Many of the familiar state-of-the-art methods are unsuitable for these calculations. Any of the calculation methods based on density functional theory (DFT) can calculate the properties of the ground state, but they are not designed for excited state calculations. Many of the calculation methods based on Hartree–Fock (HF) approximations, although capable in principle of calculating excited states, have severe convergence problems when these are attempted. At present, these considerations severely limit the classes of problems and the methods of calculation that can be treated by this theory. Fortunately, it is possible to use simpler self-consistent methods based on HF and LDA approaches.

4. An illustration of the use of the frozen Gaussian method

A core exciton is created in diamond when an X-ray of approximately 285 eV is absorbed by a 1 s electron, promoting it to the conduction band [11]. The excited state is therefore very similar to a nitrogen substitutional atom in diamond [12] — a very deep donor which has a very large trigonal distortion. Hence, one would expect the core exciton to have a substantial Stokes shift; it is estimated to be as large as 5 eV [13].

The core exciton in diamond has been modelled using the molecular dynamics code CHEMOS [14] in which the nuclei follow classical trajectories on adiabatic potential energy surfaces calculated self-consistently within the CNDO approximation. The diamond cluster we use consists of 65 carbon atoms of which the central 29 are free to move and the outer 36 are fixed. The creation of the core exciton is modelled by introducing an extra electron into the conduction band and replacing the C core by N. The runs were started from different initial nuclear configurations in order to perform the classical average over nuclear phase space.

An approximate nuclear wave function $\chi(t, R)$ was constructed consisting of the product of Gaussians of the form of Eq. (5). We used one Gaussian per atomic degree of freedom. The sum over starting configurations was made by selecting a number of sets of atomic positions. For the absorption spectra, these configurations were produced by displacing each atom a random, but small distance from its equilibrium in the ground state and introducing a small random momentum to each atom. For the emission spectra the atoms were displaced from their excited state equilibrium positions.

The time dependence of the overlap of the Gaussian wave functions on the initial and final state potential energy surfaces depends upon the widths of the Gaussians and the relaxation of the system upon excitation. We have chosen a width consistent with the frequency of the dominant mode in the cluster namely 60 meV for both the ground and excited states. We selected several values for the Gaussian width to verify that this choice has little effect upon the lineshape function.

To obtain an accurate Fourier transform of the correlation function care must be taken to have a sufficiently long simulation. In this work the period of the oscillatory component was about 60 fs, whereas data was collected every 0.25 fs so that the numerical integration of the action integral was sufficiently accurate. The simulations ran for 0.5 ps, to give a resolution in the Fourier transform, and hence in the spectra, of 8.3 meV.

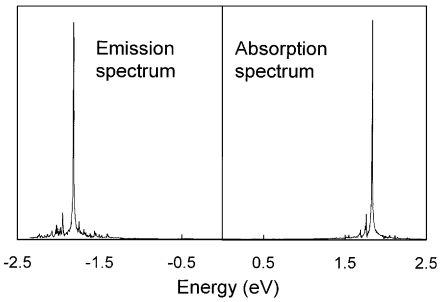

Fig. 1. The spectra calculated by the FGA technique, associated with the creation and destruction of a core exciton in diamond.

5. Results

Fig. 1 illustrates the spectrum corresponding to (a) the creation and (b) subsequent destruction of a core exciton. The absorption peak is obtained from the average over five runs and the emission peak from the average over four runs, where each run has a different set of initial positions and momenta.

The important features of the spectrum are the separation of the absorption and emission spectrum, the existence and position of the side bands on each peak and the origin of the finite width of the peaks. The separation of the peaks should correspond to the Stokes' shift, which is defined as the difference between the absorption and emission energies from the relaxed ground and excited states, respectively. The Stokes' shift as measured from the simulation data is 3.64 eV. This is in fully satisfactory accord with experimental estimates of "up to 5 eV" [13]. The spacing of the side bands seen in Fig. 1 correspond to about 70 meV and are the harmonic overtones associated with the breathing mode-like vibration. Experimentally, these would need special methods to detect.

6. Discussion and conclusion

The frozen Gaussian technique has been applied to obtain the line shapes corresponding to the creation and destruction of the core exciton in diamond. To judge the quality of the result it is necessary to compare it with experimental spectra. However, the experimental spectra have insufficient resolution for any but the most crude comparisons to be possible. The Stokes shift agrees well, but the finer structure that are predicted by this simulation are not resolved in the experimental spectra.

There are no numerical difficulties in implementing the FGA for a system of this size; it should prove to be extremely suitable for application to condensed matter problems. The problem is that most of the methods of calculating PES are not, at present, suitable for dynamic runs on excited states. The method used here, based on a particular form of self-consistent molecular dynamics, is fully adequate for demonstration purposes, or for scoping a problem, but does not achieve the accuracy of which the frozen Gaussian method is capable.

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