

PATH INTEGRAL METHODS FOR SIMULATING ELECTRONIC SPECTRA^{*}

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A new method for determining electronic absorption and emission spectra is presented. It is based on the path integral evaluation of the appropriate time correlation functions. The major advantages of this approach are (a) it is easy to obtain high-resolution spectra, (b) one can easily treat cases where the transition moment depends on nuclear configuration, i.e. the Condon approximation can be relaxed. The efficacy of the method is demonstrated by obtaining the electronic absorption spectra for two displaced Morse oscillators.

Recently we have shown [1,2] how time correlation functions of quantum systems can be determined using path integral techniques [3]. Here we show how one of these techniques [2] can be used to determine electronic absorption and emission spectra at finite temperatures. This offers a simple and more accurate alternative to wavepacket dynamics.

In the electric dipole, Franck-Condon approximation the spectrum $\bar{I}_{if}(\omega)$ corresponding to a transition from electronic state $|i\rangle$ to $|f\rangle$ given an equilibrium thermal distribution of the vibrational sites in $|i\rangle$ is proportional to

$$\bar{C}_{if}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) C_{if}(t), \quad (1)$$

$$C_{if}(t) = \text{Tr} \hat{\rho}^{(i)} \mu_{if}(\mathbf{R}) \exp(i\hat{H}_i t/\hbar) \times \mu_{fi}(\mathbf{R}) \exp(-i\hat{H}_i t/\hbar), \quad (2)$$

where the transition dipole moment, $\mu_{if}(\mathbf{R})$ depends on the internal nuclear coordinates \mathbf{R} , \hat{H}_i and \hat{H}_f are respectively the Hamiltonians of the electronic potential surfaces $|i\rangle$ and $|f\rangle$, $\hat{\rho}^{(i)} = \exp(-\beta\hat{H}_i)/\text{Tr} \exp(-\beta\hat{H}_i)$ is the density operator for the rot-vib states on the electronic surface $|i\rangle$, $\beta = (kT)^{-1}$ where k is Boltzmann's constant and T is the temperature, and $\text{Tr}(\dots)$ denotes the trace over these rot-vib states.

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Following the approach presented in our previous publication [2] we introduce the function

$$G_{if}(t) = \text{Tr} \mu_{if}(\mathbf{R}) \cdot \exp(-\hat{H}_f \tau) \mu_{if}(\mathbf{R}) \exp(-\hat{H}_i \tau^*), \quad (3)$$

where $\tau = \frac{1}{2}\beta - it/\hbar$ and τ^* is the complex conjugate of τ . It can be shown that $C_{if}(t)$ and $G_{if}(t)$ satisfy the relationship

$$C_{if}(t) = G_{if}(t - \frac{1}{2}i\beta\hbar) \quad (4a)$$

and consequently that the Fourier transforms $\bar{C}_{if}(\omega)$ and $\bar{G}_{if}(\omega)$ of $C_{if}(t)$ and $G_{if}(t)$ respectively, are related by

$$\bar{C}_{if}(\omega) = \exp(\frac{1}{2}\beta\hbar\omega) \bar{G}_{if}(\omega). \quad (4b)$$

As discussed elsewhere [2,4] $C_{if}(t)$ is difficult to determine whereas $G_{if}(t)$ can be determined directly by path integral techniques. To proceed we express $G_{if}(t)$ in the position representation

$$G_{if}(t) = \int d\mathbf{R}' \int d\mathbf{R} \mu_{if}(\mathbf{R}') \cdot \mu_{if}(\mathbf{R}) \times \langle \mathbf{R} | \exp(-\hat{H}_f \tau) | \mathbf{R}' \rangle \langle \mathbf{R}' | \exp(-\hat{H}_i \tau^*) | \mathbf{R} \rangle. \quad (5)$$

In previous papers we showed how Green's operators, $\langle \mathbf{R} | \exp(-\hat{H}\tau) | \mathbf{R}' \rangle$, can be determined using an iterative scheme starting with the short-time (semiclassical) approximation [2,5]. We call this method NMM [5]. In addition we outlined a scheme for evaluating such propagators by path integral Monte Carlo techniques [2]. Once these propagators are determined it is a

simple matter to evaluate the spectrum for any function, $\mu_{if}(R)$, so that the Condon approximation, $\mu_{if}(R) = \mu_{if}(R_e)$ need not be made (here R_e are the equilibrium positions of the nuclei).

For simplicity we ignore rotational transitions and consider a model diatomic molecule discussed by Reimers et al. [6].

The potential surfaces are displaced Morse oscillators

$$V_i(R)/\hbar\omega_i = D[1 - \exp(-\alpha R)]^2, \quad (7a)$$

$$V_f(R)/\hbar\omega_f = D\{1 - \exp[-\alpha(R - R_0)]\}^2 + D_0, \quad (7b)$$

where $\alpha = 0.1$, $D = 50$, $D_0 = 50$, $R_0 = 3$ and $\beta\hbar\omega_i = 1$. This is exactly the problem considered by Reimers et al. [6].

In the NMM method $P = 256$. The range is $(-6, 15)$. We calculate the spectra in the Condon approximation $\mu_{if}(R) = \mu_{if}(R_e) = \text{const.}$ and in the approximation $\mu_{if}(R) = \text{const.}(R - R_e)$. For purposes of comparison with Reimers et al. [6] we calculate the absorption cross section $\sigma_{if}(\omega)$,

$$\sigma_{if}(\omega) = (2\pi/3\hbar c)\omega\bar{C}_{if}(\omega). \quad (8)$$

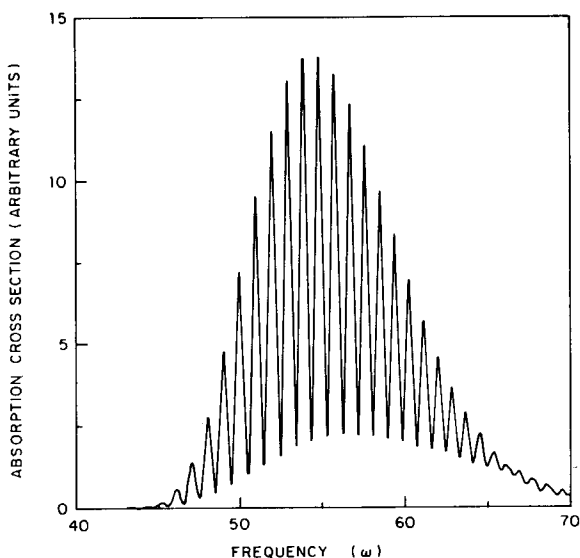


Fig. 1. Absorption cross section versus frequency (reduced units) for two displaced Morse oscillators. The parameters of the potentials are given in the text. The transition dipole operator $\mu_{if}(R)$ is taken to be a constant (Condon approximation) equal to 1 D.

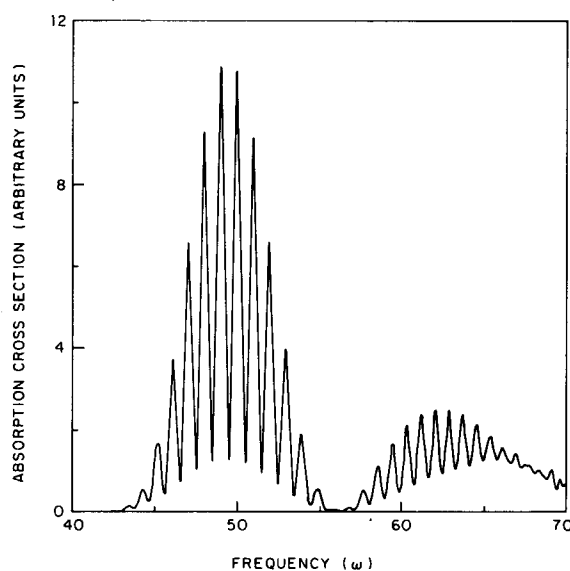


Fig. 2. Same as fig. 1 except the transition dipole operator $\mu_{if}(R) = R - R_e$.

Fig. 1 shows $\sigma_{if}(\omega)$ calculated in the Condon approximation as a function of ω . The results are in excellent agreement with the exact analytical calculations presented by Reimers et al. [6]. Fig. 2 shows the electronic absorption spectra obtained using $\mu_{if} \propto (R - R_e)$. For this case Reimers et al. [6] calculated the band contour of $\sigma_{if}(\omega)$ using Gaussian wavepacket dynamics by Fourier transforming only the initial decay of $C_{if}(t)$. Because of the truncation after short times they are not able to observe any structure in the spectrum but they note that anharmonicity in the wavepacket propagation become more severe when the Condon approximation is relaxed. We note that the detailed band contour of fig. 2 is in very good agreement with the exact analytical result reported in ref. [6]. In addition because our method is stable when applied to arbitrary potentials and dipole moments we can obtain $C_{if}(t)$ for long times. Thus we are able to resolve the detailed structure of the absorption or emission bands. Comparing figs. 1 and 2 it is obvious that relaxing the Condon approximation yields qualitatively different absorption cross sections.

Before closing this section a few comments about the possible difficulties of this method should be noted. In order to improve the spectral resolution it is necessary to determine $G_{if}(t)$ at long times. This re-

quires very large values of P . However in systems with many degrees of freedom (like condensed phases) the correlation function may decay rapidly and hence this may not be a source of difficulty. When dealing with many degrees of freedom, however, NMM in its present form cannot be used. We are presently trying to develop Monte Carlo methods for these systems.

Conclusions. In this note we have presented a new way of determining electronic spectra using path integral. The principle advantages are that this method can be applied to arbitrary potentials to calculate time correlation functions for long times and high-resolution spectra. Furthermore spectra can be calculated for any functional form of the transition dipole operator and hence the usual Condon approximation need not be made. In fact a single calculation can yield spectra for any number of functional forms for the transition dipole operators. We also note that this

method may lend itself to Monte Carlo simulations of more complex systems [2,4][‡].

[‡] After this work was completed we received a manuscript by R.D. Coalson also how the NMM method [1,2] can be applied to determine electronic absorption and emission spectra, as well as Raman spectra.

References

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