

## On the development of many-body theories for intramolecular dynamics

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**Abstract.** The efficacy of using time-dependent generalizations of the closed shell coupled cluster method for intramolecular processes associated with non-degenerate vacuum in the context of molecular absorption spectra is examined. Since the separability requirements are built into such an ansatz for the time evolution operator, it is possible to develop approximations which can take into account any number of modes, with much less computational effort than in a calculation by basis set expansion.

**Keywords.** Coupled cluster method; intramolecular dynamics; time-dependent generalizations.

### 1. Introduction

The calculation of molecular optical processes in large anharmonic molecules is one of the fundamental problems in molecular spectroscopy. Recent experimental studies on ultra-cold molecules in supersonic beams are yielding accurate information (Smalley 1982, 1983; Levy 1980, 1981), and these in turn have spurred a large number of theoretical studies on this subject (e.g. Heller 1981a, Mukamel 1985).

The analysis of spectra of isolated molecules is traditionally made in terms of molecular vibronic eigenstates (Herzberg 1966). For example, the expression for the molecular absorption spectra reads

$$P(\omega) = \sum |\langle \psi_n | \mu | \psi_g \rangle|^2 \delta(\epsilon_n - \epsilon_0 - \omega). \quad (1)$$

Here  $P(\omega)$  is the intensity,  $\psi_n$  and  $\epsilon_n$  are the vibronic states of the upper electronic states and their energies,  $\psi_g$  is the ground state of the lower surface and  $\mu$  is the dipole operator. Calculation of absorption spectrum from (1) requires an accurate knowledge of  $\psi_n$  and  $\epsilon_n$ . For small molecules it is possible to diagonalize the vibrational part of the Hamiltonian on the excited state surface. However, such a procedure is impractical for intermediate to large molecules. In order to overcome this problem, methods based on the correlation functions were developed to calculate the molecular spectra (Mukamel 1982a, b, 1984, 1985; Heller 1981a, b; Reimers *et al* 1983; Coalson and Karplus 1982, 1983; Noid *et al* 1981; Islampour and Mukamel 1984a, b; Berne and Harp 1970; Gordon 1968). Within the framework of Born-Oppenheimer approximation, and assuming that the dipole operator depends

only weakly on the nuclear coordinates, (1) may be rewritten for a single excited electronic state in the form of an autocorrelation function as follows:

$$P(\omega) = \mu_{eg} \int_{-\infty}^{\infty} \langle \phi_g(0) | \phi_g(t) \rangle \exp(i\omega t) dt. \quad (2)$$

Here,  $\mu_{eg}$  is the matrix element of the dipole operator between the ground and excited electronic states,  $\phi_g$  is the vibrational ground state of the lower surface, and,

$$|\phi_g(t)\rangle = \exp(-iH_u t) |\phi_g(0)\rangle, \quad (3)$$

where  $H_u$  is the vibrational Hamiltonian of the upper surface.

Several approximations, based upon classical and semiclassical mechanics have been developed to calculate the auto-correlation functions for large systems and tested on a few model systems (Heller 1981b; Mukamel 1982a; Warshel *et al* 1983).

In the present communication we develop a fully quantum-mechanical theory for the description of intramolecular dynamics and the calculation of auto-correlation functions based on the time-dependent coupled cluster method. Since the separability requirements of many particle systems are built into any ansatz based on the coupled cluster method, it is possible to develop approximations to the time evolution operator (and thus to the correlation functions) which can take into account any number of modes with much less computational effort than in a calculation by basis set expansion. Section 2 contains the theoretical development of our work and §3 the concluding remarks.

## 2. Theory

The molecular vibrational Hamiltonians are given in normally ordered form, as

$$H(\alpha) = \sum \omega_{ij}(\alpha) a_i^\dagger a_j + \sum V_{mn}^{ij}(\alpha) (a_i^\dagger)^m (a_j)^n + \dots \quad (4)$$

Here  $\alpha$  is the index of the electronic state,  $a_i^\dagger$ ,  $a_i$  are the usual creation and annihilation operators of the  $i$ th mode,  $\omega_{ij}$  are the frequencies, and  $V_{mn}^{ij}$  etc. are the various anharmonic coupling constants. We define the origin of the molecule fixed coordinate frame at the minimum of the ground electronic surface and expand the potential energy  $V(\alpha)$  in terms of the normal coordinates of that state. Since the anharmonicity terms rarely affect the vibrationless state to any appreciable extent, we can approximate the doorway state  $|\phi_g\rangle$  as

$$|\phi_g\rangle = |0\rangle, \quad (5)$$

where  $|0\rangle$  is the vacuum state for the operators  $a_i$ .

The time development of the vacuum state is given by the coupled cluster ansatz in a normal ordered form as

$$\begin{aligned} |t\rangle &= \exp(-iH_u t) |0\rangle \\ &= \exp(S) |0\rangle, \end{aligned} \quad (6)$$

where,

$$S = S_0 + S_1 + S_2 \dots, \quad (7a)$$

$$S_1 = \sum_i s_i^1 a_i^\dagger, \quad (7b)$$

$$S_2 = \sum_{ij} s_{ij}^2 a_i^+ a_j^+, \quad (7c)$$

$$S_3 = \sum_{ijk} s_{ijk}^3 a_i^+ a_j^+ a_k^+. \quad (7d)$$

and  $S_0$  is a complex scalar.

The equations for the cluster amplitudes  $s^n$  are obtained from the time-dependent Schrödinger equation. In atomic units

$$i \frac{\partial}{\partial t} |t\rangle = H_u |t\rangle. \quad (8)$$

Substituting (6) into (8), premultiplying by  $\exp(-S)$  and projecting onto different excited states  $|m\rangle$  we obtain,

$$i\dot{s}_m = \langle m | \bar{H}_u | 0 \rangle. \quad (9)$$

Here,

$$\bar{H}_u = \exp(-S) H_u \exp(S). \quad (10)$$

Equations (10) and (11) are the working equations in the present theory. In general the expressions for  $\bar{H}_u$  are non-linear in the amplitudes  $s_m$  and have to be numerically integrated, subject to the initial value conditions,

$$s_m(0) = 0. \quad (11)$$

This is required since in the doorway state picture excitation to the upper surface occurs at  $t = 0$ .

The auto-correlation function is given by

$$\langle t | 0 \rangle = \exp(S_0) \quad (12)$$

where  $S_0$  is given by

$$i\dot{S}_0 = \langle 0 | \bar{H}_u | 0 \rangle. \quad (13)$$

Using (12) spectral bands of any surface can be calculated via (2).

Since the working equations (9) give full information regarding the time evolution operator, they can be used for the description of intramolecular dynamics. For example, the energy in the  $i$ th mode  $E_i$ , at any time  $t$ , is given by

$$\begin{aligned} E_i(t) &= \omega_i \frac{\langle 0 | \exp(S^+) a_i^+ a_i \exp(S) | 0 \rangle}{\langle 0 | \exp(S^+) \exp(S) | 0 \rangle} \\ &= \omega_i \langle 0 | \exp(S^+) a_i^+ a_i \exp(S) | 0 \rangle_{\text{linked}}. \end{aligned} \quad (14)$$

Here the last line follows from the linked cluster theorem of exponential ansatz (Pal *et al* 1982).

### 3. Concluding remarks

The main problem in a conventional approach to the calculation of optical spectra of large molecules is the dimensions of the matrices to be constructed and

diagonalized. This has led to the development of time-dependent approaches. As Heller (1981a) observed, for a frequency resolution of a few tens of wave numbers, the correlation function needs to be evaluated for a few picoseconds only. Thus the spectral band calculation reduces to the analysis of short-time intramolecular dynamics.

The present work was concerned with the development of the time-dependent coupled cluster method for the description of intramolecular dynamics. There are several advantages in the present approach. First, since the cluster amplitudes are continuous complex variables, this approach may be viewed as a quantum trajectory method, and thus, does not suffer from the limitations of the conventional basis set expansion methods. We recall, in this context, that a displaced harmonic oscillator function is represented as

$$\begin{aligned} |\phi_d\rangle &= \exp(da^+ - d^*a)|0\rangle \\ &= \exp\left(da^+ + \frac{dd^*}{2}\right)|0\rangle. \end{aligned} \quad (15)$$

Thus in the approximation  $S = S_0 + S_1$ , the ansatz (6) is just a travelling Gaussian function. It can be shown in a similar fashion that inclusion of  $S_2$  takes into account, the changes in the effective force constants and frequencies. For general harmonic surfaces, (9) and (10) form a closed set with  $S = S_0 + S_1 + S_2$ , a feature they share with the semiclassical theories (Heller 1981a; Mukamel 1982a).

Being a fully quantum mechanical theory, the present approach has no problems in the calculation of the phase accumulated during the propagation (which is absorbed into  $S_0$ ) nor does it need any additional corrections such as uniformization in the case of degeneracies. Because of these features, it is superior to the semiclassical theories. Also it does not require the calculation of overlap function  $\langle t|0\rangle$  at each instant, as required in the Frozen Gaussian approach, of Heller (1981b), which is a considerable saving computationally.

In the present form, the time-dependent coupled cluster theory is limited to the dynamics of a vacuum state. Extensions to higher states are necessary before it can be applied to general intramolecular processes. Work is in progress in this direction, and shall be reported in due course.

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