

Calculation of the electronic spectra of molecules in solution and on surfaces

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Abstract

An approach is presented to calculate the electronic spectra of molecules in solution or adsorbed on surfaces. Through limiting electronic excitations to include only those between orbitals localized on the solute or adsorbant, large computational savings are achieved with minimal additional error. This approach has been implemented within time-dependent density functional theory and single excitation configuration interaction. Calculations of the electronic spectrum of formamide in water and carbon monoxide on the Ni(111) surface illustrate the method.

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1. Introduction

The calculation of molecular electronic spectra is well established [1,2] and excitation energies can be determined to within a few tenths of an electron volt. This can be achieved using wavefunction methods, such as multi-configurational perturbation theory or time-dependent density functional theory (TDDFT) [2,3]. However, this success is generally limited to the study of isolated or ‘gas-phase’ molecules. Much of chemistry and biology occurs in solution or on surfaces. The molecular environment can have a profound effect on electronic structure and can change chemical behaviour [4]. Consequently, predicting and understanding the influence of solvent or a surface represents a fundamental problem in chemistry and a challenge for theory.

Theoretical treatment of electronic spectra in solution has received considerable attention, and a number of approaches are widely used. The most common approach adopts a simple model in which the solute is considered to be in a cavity embedded in a macroscopic continuum medium [5,6]. This model has been successful in the study of a number of systems [7]; however, potentially serious deficiencies remain. The neglect of

specific solute–solvent interactions, such as hydrogen bonds, can often result in large errors. Ideally, a model should include many solvent molecules and also account for the numerous configurations that characterize the statistical nature of the solvent. This requires a combination of molecular dynamics simulations and quantum chemical calculations. Car–Parrinello molecular dynamics coupled with TDDFT theory provide a fully quantum mechanical description [8,9]. The cost of these calculations can be reduced through a classical description of the solvent. This can be achieved in a hybrid or sequential quantum mechanics/molecular mechanics (QM/MM) approach. In a hybrid scheme the classical and quantum mechanical regions are interfaced directly [10,11], while a sequential approach uses structures generated from a MM simulation for subsequent use in QM calculations. The sequential QM/MM approach has been used extensively in conjunction with semi-empirical quantum chemical methods [12–15]. While many solvent molecules may be included, only shifts and not actual spectra can be predicted accurately. A reduction in the cost of the QM part of the calculation would extend sequential QM/MM approaches to the study of large molecules in solution incorporating many solvent molecules using accurate ab initio methods. Furthermore, the inclusion of solvent within the QM region of hybrid schemes could be achieved more readily.

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The calculation of the electronic spectra of molecules adsorbed on surfaces presents similar problems to calculations in solution, but fewer studies have been reported. Mochizuki et al. [16] proposed a scheme based on the configuration interaction with single excitations (CIS) method. The number of configurations was reduced by removing excitations to the virtual orbitals of the metal surface atoms. In the approach of Klüner et al. [17,18], a small cluster consisting of the adsorbed molecule and a small number of metal atoms is embedded within a periodic DFT framework. The cluster is treated using complete-active-space self-consistent-field method with the effect of the environment treated via a one-electron embedding potential. In the method reported by Corni and Tomasi [19] the metal surface is treated as a continuous body, characterized by a dielectric constant.

The rapid rise in the computational cost of such calculations within traditional CIS or TDDFT methods is in part due to the large number of electronic excitations associated with the solvent molecules or surface atoms. However, these excitations are generally of much less interest. In this Letter, we describe an approach that avoids this problem by performing the excited state calculation within a subset of electronic excitations between orbitals associated with the solute or adsorbed molecule. An additional benefit is the excited states become much easier to assign. This approach is similar in spirit to the work of Mochizuki et al. [16], and has been implemented within a development version of the Q-Chem software package [20] for CIS and TDDFT methods.

2. Theoretical approach

Detailed accounts of the working equations of TDDFT are given elsewhere [1,21,22], and only a brief description is given here. Excitation energies can be obtained from the poles and residues of the dynamic polarisability. They can be determined as the solutions of the non-Hermitian eigenvalue problem

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}, \quad (1)$$

where the matrices \mathbf{A} and \mathbf{B} are given by

$$A_{a i \sigma, b j \tau} = \delta_{ij} \delta_{ab} \delta_{\sigma\tau} (\varepsilon_{a\sigma} - \varepsilon_{i\tau}) + K_{a i \sigma, b j \tau}, \quad (2)$$

and

$$B_{a i \sigma, b j \tau} = K_{a i \sigma, j b \tau}. \quad (3)$$

The convention of i, j, \dots denoting occupied orbitals and a, b, \dots denoting virtual orbitals is adopted, while σ and τ are spin indices. \mathbf{X} and \mathbf{Y} describe the linear response of the Kohn–Sham density matrix in the basis of the unperturbed molecular orbitals and ε_i are the orbital energies. \mathbf{K} is the coupling matrix, and is given by

$$K_{a i \sigma, b j \tau} = \left(\psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}) \middle| \psi_{j\tau}^*(\mathbf{r}') \psi_{b\tau}(\mathbf{r}') \right) + \int d\mathbf{r} d\mathbf{r}' \psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}) \frac{\delta^2 E_{\text{XC}}}{\delta \rho_{\sigma}(\mathbf{r}) \delta \rho_{\tau}(\mathbf{r}')} \psi_{j\tau}^*(\mathbf{r}') \psi_{b\tau}(\mathbf{r}'), \quad (4)$$

where E_{XC} is the exchange correlation functional. Within the Tamm–Dancoff approximation (TDA) [22], Eq. (1) reduces to the Hermitian eigenvalue equation

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}. \quad (5)$$

Formally CIS is similar to TDDFT/TDA, but has a different coupling matrix \mathbf{K} . For CIS, \mathbf{K} has the form

$$K_{a i \sigma, b j \tau} = \left(\psi_{a\sigma}^*(\mathbf{r}) \psi_{i\sigma}(\mathbf{r}) \middle| \psi_{j\tau}^*(\mathbf{r}') \psi_{b\tau}(\mathbf{r}') \right) - \left(\psi_{a\sigma}^*(\mathbf{r}) \psi_{b\tau}(\mathbf{r}) \middle| \psi_{j\tau}^*(\mathbf{r}') \psi_{i\sigma}^*(\mathbf{r}') \right). \quad (6)$$

The only difference in the calculation of CIS and TDDFT/TDA excitation energies lies in the exchange-type integrals used in the formation of the \mathbf{A} matrix [22]. In the implementation within Q-Chem, excitation energies are evaluated using the iterative subspace algorithm of Davidson [23]. Initially a trial set of vectors consisting of a minimum number of the lowest energy single excitations is constructed. The matrix \mathbf{A} is projected onto this subspace and the smaller eigenvalue problem is solved. These eigenvalues and vectors are approximations to the solution of the full eigenvalue problem. The method then proceeds iteratively. For each excited state required that has not converged, a correction vector is constructed and added to the subspace of single excitations. This process continues until all the required excited states have converged.

In order to reduce the rise in computational cost for calculations of the electronic spectrum of molecules in solution or on surfaces, we limit the subspace of excitations to include only excitations between orbitals associated with the solute or adsorbed molecule. The following eigenvalue equation is solved

$$\bar{\mathbf{A}}\mathbf{X} = \omega\mathbf{X}, \quad (7)$$

where

$$\bar{\mathbf{A}} = A_{\bar{a}i\sigma, \bar{b}j\tau}, \quad (8)$$

and $\{\bar{i}\}$ and $\{\bar{a}\}$ are subsets of occupied and virtual orbitals, respectively. This scheme is incorporated within the current implementation by constructing initial trial vectors from the truncated subset of single excitations formed from excitations between $\{\bar{i}\}$ and $\{\bar{a}\}$. The Davidson procedure is used as before, except that the correction vector is projected onto the subspace formed by the truncated set of single excitations and renormalized. This approximation is applicable when a subset of electronic excitations is of interest and these excitations are only weakly coupled to the remaining excitations.

A remaining problem is the selection of the occupied and virtual orbital subspaces. It is desirable to select the appropriate orbitals in a predetermined way without a priori knowledge of the Hartree–Fock orbitals of the system. In our implementation, the occupied orbitals are selected based on their Mulliken populations [24]. If a set of atoms is specified, then basis functions associated with these atoms constitute a subset of the basis functions, $\{\bar{\lambda}\}$. κ_i^{occ} is defined such that

$$\kappa_i^{\text{occ}} = \sum_{\bar{\lambda}} M_{\bar{\lambda}i}, \quad (9)$$

where $M_{\bar{\lambda}i}$ is the contribution to the Mulliken population of orbital i from basis function $\bar{\lambda}$. Thus κ_i^{occ} provides a measure of the atoms on which orbital i is localized. All κ_i^{occ} are evaluated; if κ_i^{occ} is greater than a user defined value (between 0 and 2 for restricted CIS or TDDFT) then orbital i is included in $\{\bar{i}\}$. A similar scheme based on the normalized molecular orbital coefficients is used for the virtual orbitals.

$$\kappa_a^{\text{vir}} = \sum_{\bar{\lambda}} |c_{\bar{\lambda}a}|^2. \quad (10)$$

Similarly, if κ_a^{vir} is greater than another user defined parameter (between 0 and 1) a is included in $\{\bar{a}\}$. This has been implemented in Q-Chem [20] for CIS and TDDFT/TDA. The only additional input required is the atoms that constitute the solute or adsorbant and the occupied and virtual orbital cutoffs.

3. Numerical applications

The role of amides as a model of the repeating unit in protein backbones has made their electronic structure of considerable interest [15,25–27]. Strong inter-molecular

hydrogen bonds form between formamide and water molecules. In many respects this represents a severe test of the method described here. Consequently, formamide in water is an excellent system to examine.

Table 1 shows the computed excitation energies for a complex of formamide and four water molecules. This complex was extracted from a molecular dynamics simulation with the four closest water molecules to the formamide molecules retained. Atomic coordinates can be obtained from the author on request. TDDFT/TDA excitation energies obtained with the B3LYP functional [28] are presented. The 6-31++G** and 6-31++G basis sets are used for formamide and water, respectively. The results of three different calculations are shown. In the first calculation no truncation of the occupied or virtual orbital subspaces has been made. In addition to the formamide excited states, a number of formamide \rightarrow water charge transfer (CT) excitations are observed. These can occur at relatively low energies. Furthermore, a large number of CT water \rightarrow formamide and intra-molecular water \rightarrow water excitations are observed. Although not shown, they typically occur in the 6–7 eV region. In the second calculation the occupied orbital subspace is limited to the 12 formamide orbitals. These are easily selected using Mulliken populations. Typically, κ_i^{occ} of 0.5 (1.0 within the restricted formalism) will retain just the formamide occupied orbitals, Eq. (9). In this calculation the intra-molecular water and water \rightarrow formamide CT excitations are no longer observed. In the remaining calculation, truncation of the occupied and virtual orbital subspaces is used. The more diffuse nature of virtual orbitals makes their selection more difficult. In these calculations, κ_a^{vir} of 0.4 is used. This retains the majority (106 of 119) of the virtual orbitals while rejecting any low-lying virtual orbitals of the

Table 1
Calculated TDDFT/B3LYP formamide \cdot 4H₂O excitation energies (in eV) and oscillator strengths in parentheses

Transition	No restriction of orbitals	Restriction of occupied orbitals	Restriction of occupied and virtual orbitals
n π^*	5.72 (0.00)	5.92 (0.00)	5.93 (0.01)
^a n \rightarrow w	6.12 (0.01)	6.13 (0.01)	–
$\pi \rightarrow$ w	6.26 (0.01)	6.26 (0.01)	–
n3s	6.99 (0.01)	6.97 (0.03)	6.98 (0.03)
π 3s	7.10 (0.03)	7.11 (0.03)	7.12 (0.03)
$\pi\pi^*$	7.35 (0.12)	7.38 (0.12)	7.41 (0.09)
n3p	7.55 (0.06)	7.56 (0.06)	7.60 (0.14)
n \rightarrow w	7.59 (0.01)	7.63 (0.07)	–
π 3p	7.69 (0.01)	7.68 (0.01)	7.68 (0.01)
$\pi \rightarrow$ w	7.80 (0.01)	7.79 (0.01)	–
n3p	8.15 (0.02)	8.15 (0.02)	8.15 (0.02)
π 3p	8.32 (0.01)	8.31 (0.01)	8.31 (0.01)
n3p	8.34 (0.02)	8.33 (0.01)	8.34 (0.02)
π 3p	8.49 (0.02)	8.39 (0.02)	8.39 (0.02)
Maximum subspace	280	159	151
Mean absolute error (eV)	N/A	0.04	0.04
Time (s)	2222	1521	1487

^a n \rightarrow w denotes a charge transfer transition from the formamide n orbital to a water molecule.

water molecules, and only the intra-molecular formamide excitations remain.

The agreement between the excitations from the full TDDFT and truncated calculations is good. For both calculations the mean absolute error is 0.04 eV. Most of this error occurs for the $n\pi^*$ excitation. This is not surprising since this transition undergoes a large blue-shift due to hydrogen bonding [27]. This is reflected in κ_i^{occ} of the orbitals. For core orbitals $\kappa_i^{\text{occ}} > 1.95$, indicating negligible contribution from the solvent orbitals. For the valence orbitals κ_i^{occ} is lower, particularly for the n orbital where $\kappa_i^{\text{occ}} \approx 1.2$. For this orbital there is a relatively large contribution from orbitals associated with the hydrogen atom of the neighbouring solvent molecule. Inclusion of an additional occupied orbital of the closest water molecule removes the error in the $n\pi^*$ excitation energy. Since only the orbitals of the nearest solvent may have a significant mixing with solute orbitals, this error does not continue to increase with additional solvent.

While information about solute-solvent charge transfer excitations is lost, such excitations could be included within the formalism by including orbitals from neighboring solvent molecules within $\{\bar{i}\}$ and $\{\bar{a}\}$. TDDFT in conjunction with local exchange-correlation functionals do not provide a correct description of CT transitions [29]. Recent work [8] suggests that these transitions are the source of spurious results in the calculation of the $n\pi^*$ transition in acetone. Consequently, their omission may be beneficial. Restriction of the occupied space has little effect on the computed intensities of the transitions. However, the intensities are more sensitive to restriction of the virtual orbitals, in particular the relative strengths of the $\pi\pi^*$ and $n3p$ excitations.

Substantial computational savings are gained, as a result of the reduction in the size of the A matrix that needs to be diagonalised. The sizes of the excitation subspace on the final iteration (Table 1) show a reduction by nearly a factor of two. The overall cost of the TDDFT calculation will depend on the number of iterations required in addition to the size of A . The results show that the time of the calculation is reduced by approximately 25%. All timings refer to calculations performed using a desktop PC with an Intel 2.0 GHz processor and 1 GB of memory. The relative size of computational savings will grow with the number of water molecules. Fig. 1 shows the time for the TDDFT calculations as the number of water molecules is increased. These times reflect the time to compute the electronic spectrum up to ~ 9 eV. This captures the low-lying valence and Rydberg states. If no truncation is made, the cost of the calculation rises steeply beyond four water molecules and memory constraints prevented the inclusion of more than seven waters. Truncation of the excitation subspace prevents this steep rise and many more water molecules can be included. Additional

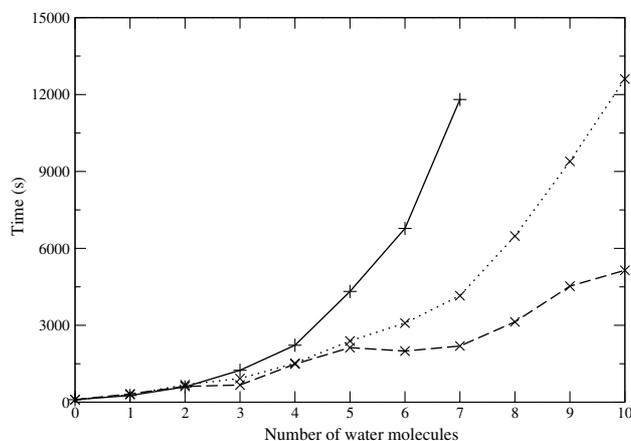


Fig. 1. Time for formamide + water calculation. Solid line – no truncation, dotted line – truncation of occupied orbitals, dashed line – truncation of occupied and virtual orbitals.

truncation of the virtual orbital subspace provides further significant savings. In general, the computational savings will depend on the nature of the electronic excitations in the solvent and solute. For computational savings to be gained the solvent must have electronic excitations that lie lower than the solute electronic excitations of interest. Consequently, this approach will be advantageous when relatively high-lying excitations are required or for electronic spectra in solvents with low-lying excitations.

The adsorption of carbon monoxide on transition metal surfaces, a prototypical system in surface science, has been studied extensively. Electronic excitation spectra have been investigated predominantly by electron-energy-loss spectroscopy (EELS). Much of this work has been summarized by Netzer et al. [30]. There has been considerable debate over the assignment of the spectral bands. This debate primarily concerns the intra-molecular $\text{CO } ^1(5\sigma \rightarrow 2\pi^*)$ transition. This has been reported to lie at ~ 13.5 eV [31] and 8.0–9.0 eV [32,33]. Table 2 shows computed excitation energies for the intra-molecular excitations of CO on the 3-fold site of Ni(111) for CIS and TDDFT/TDA with the B3LYP functional. Results are shown for calculations in which there has been no restriction of the orbital subspaces and when only excitations from the 12 occupied orbitals of CO are allowed. The surface is modeled using a cluster consisting of three Ni atoms, and the geometry described by Wong and Hoffmann is used [34]. The 6-31++G** basis set is used for the carbon and oxygen atoms while the LANL2DZ basis set [35] is used for nickel.

This size of the error introduced by limiting the electronic excitations is small for both CIS and TDDFT, although there is some reduction in the calculated intensities of the $^1(5\sigma \rightarrow 2\pi^*)$ excitation. Computational savings for this type of system are high due to the large

Table 2

Excitation energies (in eV) and selected oscillator strengths in parentheses of CO adsorbed on Ni(111)

State	Transition	CIS	^a rCIS	B3LYP	rB3LYP
a ³ Π	³ (5σ → 2π*)	9.87	9.72	8.34	8.35
a ³ Σ ⁺	³ (1π → 2π*)	8.72	8.69	7.88	7.87
d ³ Δ	³ (1π → 2π*)	9.47	9.47	8.06	8.06
A ¹ Π	¹ (5σ → 2π*)	11.19 (0.08)	11.06 (0.04)	8.66 (0.06)	8.62 (0.04)
I ¹ Σ ⁻	¹ (1π → 2π*)	10.19	10.22	8.26	8.26
D ¹ Δ	¹ (1π → 2π*)	10.55	10.52	8.37	8.33
Mean absolute error (eV)		N/A	0.06	N/A	0.02
Time (s)		4809	374	6254	1303

^ar denotes a calculation in which excitations are restricted to those from CO occupied orbitals.

number of low-lying excitations within the metal cluster. The cost of the calculations is approximately 8% and 20% of the traditional CIS and TDDFT methods, respectively. These savings will grow as the size of the cluster model of the surface is increased. With no restriction of the electronic excitations, calculations with more than three surface atoms soon become intractable. However, when restrictions are imposed much larger surface clusters can be considered. Predicted ¹(5σ → 2π*) excitation energies are 11.19 and 8.66 eV for CIS and TDDFT, respectively. The corresponding gas-phase excitation energies are 9.28 and 8.55 eV. The large blue-shift for CIS is not observed for TDDFT. In both cases, the interaction of the 5σ orbital with the metal d orbitals results in its energy being lowered below the 1π orbitals. This gives a blue-shift for CIS. However, for TDDFT this is accompanied by a lowering of the 2π* orbitals resulting in little shift in the ¹(5σ → 2π*) excitation energy. This is consistent with earlier calculations [17,18].

4. Conclusions

In this Letter, an approach to calculating the electronic spectrum of molecules in solution or adsorbed on surfaces has been described. Within this approach the CIS or TDDFT excited state calculation is performed within a subset of the possible single excitations. Substantial computational savings are gained with the introduction of only a small error. An additional benefit is the states can be assigned easily. Using this method, quantitative calculations of the electronic spectra of molecules in solution incorporating many solvent molecules and on surfaces with extensive models of the surface can be achieved.

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