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Non-adiabatic couplings by time-dependent density functional theory

Roi Baer *

Department of Physical Chemistry and the Lise Meitner Center for Quantum Chemistry,
The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Abstract

A method is developed to compute non-adiabatic couplings (NACs) between the electronically ground and excited states of a molecule. Applying the method to the $H + H_2$ system, using the adiabatic local density approximation (ALDA), yields very good results as long as the CI is not approached too closely.

1. Introduction

The Born–Oppenheimer–Huang (BOH) approximation [1] forms a conceptual framework and jargon with which we think about molecular processes. It is motivated by the fact that nuclei are thousands of times heavier than electrons. Within this theory, electrons affect the nuclear dynamics via two types of quantities: adiabatic potential energy surfaces (PES)

$$\varepsilon_n(R) = \left\langle \psi_n | \hat{H}_e | \psi_n \right\rangle \quad n = 0, 1, \ldots, \quad \varepsilon_n \leqslant \varepsilon_{n+1} \tag{1.1}$$

and non-adiabatic couplings (NACs)

$$\tau^{\mu}_{nm} = \left\langle \psi_n | \partial_\mu \psi_m \right\rangle, \quad n, m = 0, 1, 2, \ldots \tag{1.2}$$

The latter quantities are important for detailed understanding of certain classes of biological, photochemical and other molecular processes. In the above expressions, ψ_n is a normalized eigenstate of the electronic Hamiltonian $\hat{H}_e(R) = \hat{T} + \hat{V}(R) + \hat{U}$, respectively composed of: electronic kinetic, electron–nuclear attraction and electron–electron repulsion energies. Since the electronic Hamiltonian depends on the position of the nuclei R, so do the eigenfunctions ψ_n and eigenenergies ε_n. The NACs of Eq. (1.2) are defined in terms of the partial derivative $\partial_\mu \equiv \partial / \partial R_\mu$ with respect to a Cartesian nuclear coordinate R_μ. The NACs have several notable properties. For problems without spin–orbit interactions τ^μ can be considered a real antisymmetric matrix. The sign of τ^μ_{nm} is arbitrary, although the signs of different components, for example, τ^μ_{01} and τ^ν_{01} are related. The Hellmann–Feynman theorem holds

$$\tau^{\mu}_{nm} = \frac{\left\langle \psi_n | \partial_\mu \hat{H}_e | \psi_m \right\rangle}{\varepsilon_m - \varepsilon_n}, \tag{1.3}$$

showing that the approximation, of neglecting NACs, is invalid especially in regions where ε_n approaches ε_m.

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* Fax: +972-2-651-3742.
E-mail address: roi.baer@huji.ac.il (R. Baer).

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In recent years, there is a growing experimental and theoretical interest in the effects of non-adiabatic interactions in the presence of conical intersections (CIs) [2–12]. One important conclusion is that a quantitative description of many molecular processes depends on the availability of accurate NACs. These quantities are readily accessible when the electronic structure of the system is analyzed in terms of the electronic wavefunctions. Electronic structure methods that construct the electronic wavefunction can supply the NACs via analytical derivative methods [13]. These approaches however are limited to small or medium sized systems because the electronic wavefunctions become exceedingly complicated as the number of electrons grows.

The Kohn–Sham density functional theory [14] (DFT) is a method to compute the ground potential surfaces of very large systems. It can do so because it completely alleviates explicit construction of the electronic wavefunction. Runge and Gross [15] extended the scope of DFT to time-dependent electronic processes, making excited electronic states accessible. Indeed, the resulting time-dependent density functional theory (TDDFT) is evolving to be the method of choice for studying excited electronic states of large molecules [16–23].

Despite the great success in computing adiabatic PES's the applicability of TDDFT to non-adiabatic couplings has been scarcely investigated. Chernyak et al. [24] have given closed expressions for the NACs in adiabatic and non-adiabatic versions of TDDFT. But to our knowledge, there has not yet been any attempt to actually compute via TDDFT the NACs for a specific molecular system, thus there is no experience as to the quality of such a calculation.

In this Letter we develop a method of computing NACs to the groundstate, namely $\tau^{\mu}_{0,n}$ based on real-time density functional theory. In several aspects it is similar to the method of Chernyak et al. [24], for example, it invokes linear response theory. It is different in the choice of the perturbing operator, the use of real-time TDDFT, and the method of extracting the NACs from the resulting calculation. We apply the method to $\mathrm{H} + \mathrm{H}_2$, the benchmark system for assessing the effects of a CI on reactive scattering [9,25,26].

The structure of the paper is as follows. The theory is developed in Section 2. The application to the molecular system is shown in Section 3 summarizing in Section 4.

2. Theory

2.1. The basic approach

We first perturb the system with a weak short time-dependent pulse. The response of the system is thus linear with pulse strength. Usually in such a circumstance, first-order perturbation theory is used, together with known matrix elements of the perturbing operator to compute the response of the system. We make the theory work in reverse: the exact response of the system is determined directly by the time-dependent Kohn–Sham equations and the resulting signals are then analyzed using first-order perturbation theory to obtain matrix elements.

2.2. Details of the method

The field we use couples to the system through some observable of the form $\hat{\pi} = \sum_{q=1}^{N_e} \pi(\mathbf{r}_q)$ where N_e is the number of electrons, thus the Hamiltonian controlling the time-dependent evolution of the electrons is

$$\hat{H}(t) = \hat{H}_e + \eta f(t)\hat{\pi}. \tag{2.1}$$

Here η is the field strength and $f(t)$ is a pulse of duration T

$$f(t) = \mathrm{e}^{-\frac{(t-T_0)^2}{2T^2}}. \tag{2.2}$$

A convenient choice for the perturbing operator $\hat{\pi}$ is a component of the dipole operator, for example: $\pi(\mathbf{r}) = ez$. Other observables may be used as well, the requirement is that $\hat{\pi}$ have non-vanishing matrix elements $\pi_{n0} = \langle\psi_n|\hat{\pi}|\psi_0\rangle$, where ψ_n – the coupled electronic state and ψ_0 is the ground electronic state.

The perturbation drives the system into motion resulting in a time-dependent wavefunction $\psi(t)$. Soon, the external field dies out but the motion it stirred up remains. Suppose now we 'measure' the time-dependent expectation value of another operator, say $\hat{Y} = \sum_{n=1}^{N_e} y(\mathbf{r}_n)$. Using linear response theory as [27], the signal $\Delta Y(t) = \langle \psi(t)|\hat{Y}|\psi(t)\rangle - Y_{00}$ of this operator can be written as

$$\Delta Y(t) = \frac{\eta}{\mathrm{i}\hbar} \int_0^\infty f(t-\tau)\left[\hat{Y}(\tau), \hat{\pi}\right]_{00} \mathrm{d}\tau, \tag{2.3}$$

where $\hat{Y}(\tau) = \mathrm{e}^{\mathrm{i}\hat{H}_e \tau}\hat{Y}\mathrm{e}^{-\mathrm{i}\hat{H}_e \tau}$. Expanding Eq. (2.3) in eigenstates of H_e and performing the integral yields for $t \gg T$

$$\Delta Y(t) = \frac{2\eta}{\hbar} \mathrm{Im} \sum_n Y_{0n} \pi_{n0} \mathrm{e}^{-\mathrm{i}\omega_{n0} t} f_{\omega_{n0}}, \tag{2.4}$$

where $\omega_{n0} = \varepsilon_n - \varepsilon_0$ are the excitation energies above the groundstate, $Y_{0n} = \langle \psi_0|\hat{Y}|\psi_n\rangle$, $\pi_{n0} = \langle \psi_n|\hat{\pi}|\psi_0\rangle$ and $f_\omega = \sqrt{2\pi} T \mathrm{e}^{-\mathrm{i}\omega T_0} \mathrm{e}^{-\frac{T^2\omega^2}{2}}$ is the Fourier transform of $f(t)$.

Now, assume we have computed, using TDDFT, the signal $\Delta Y(t) = \int [\rho(\mathbf{r}, t) - \rho_{gs}] y(\mathbf{r})\, \mathrm{d}^3 r$, of length $2T_f$. Let $\Delta\tilde{Y}(\omega)$ be the windowed Fourier transform of $\Delta Y(t)$:

$$\Delta\tilde{Y}(\omega) = \int_{-\infty}^{\infty} \mathrm{e}^{\mathrm{i}\omega t} \mathrm{e}^{-\frac{(t-T_f)^2}{2\sigma^2}} \Delta Y(t)\, \mathrm{d}t, \tag{2.5}$$

where $\sigma = T_f/2\pi$. Assuming the electronic Hamiltonian and the operators $Y(\mathbf{r})\pi(\mathbf{r})$ are real, it is straightforward to show that for ω in the vicinity of ω_{n0}

$$\Delta\tilde{Y}(\omega) \approx Q(\omega, \omega_{n0}) Y_{0n} \pi_{n0}, \tag{2.6}$$

where

$$Q(\omega, \omega_{n0}) = \frac{2\pi\eta T\sigma}{\mathrm{i}\hbar} \mathrm{e}^{-\frac{T^2\omega_{n0}^2}{2}} \mathrm{e}^{-\frac{\sigma^2(\omega-\omega_{n0})^2}{2}} \mathrm{e}^{-\mathrm{i}\omega_{\mathrm{n}0} T_0} \mathrm{e}^{\mathrm{i}(\omega-\omega_{n0}) T_f}. \tag{2.7}$$

This relation becomes exact in the limit of a long signal ($\sigma \to \infty$). We can now apply Eq. (2.6) twice. Once, taking $\hat{Y} = \hat{\pi}$, $\Delta\tilde{\pi}(\omega) = Q(\omega,\omega_{n0})|\pi_{n0}|^2$ and twice taking for $\hat{Y}$ the nuclear force: $y(\mathbf{r}) = F_\mu(\mathbf{r}) = -\partial_\mu V(\mathbf{r})$. From Eq. (2.3) $\Delta\tilde{F}_\mu(\omega)/\omega_{n0} = -Q(\omega, \omega_{n0}) \tau_{0n}^\mu \pi_{n0}$, which upon squaring and dividing by $\Delta\tilde{\pi}(\omega)$ yields:

$$\left|\tau_{0n}^\mu\right|^2 = \frac{\left|\Delta\tilde{F}_\mu(\omega)\right|^2}{\omega_{n0}^2 Q(\omega, \omega_{n0})^* \Delta\tilde{\pi}(\omega)}. \tag{2.8}$$

Eq. (2.8) is the central formula for determining the non-adiabatic coupling of excited states to the groundstate. One can determine ω accurately by searching for an appropriate value that renders $|\tau_{0n}^\mu|^2$ real. We summarize the procedure in the following algorithm:

Algorithm: (1) Compute the groundstate density of the molecule $\rho_0(\mathbf{r})$ (using DFT). (2) Starting from $\rho(0) = \rho_0$, solve [28,29] the time-dependent Kohn–Sham equations [15] based on the Hamiltonian of Eq. (1.1). (3) Compute the dipole component $\pi(t) = \mathrm{e} \int x\rho(\mathbf{r}, t)\, \mathrm{d}^3 r$ and the nuclear force $F_\mu(t) = -\rho(\mathbf{r}, t)\partial V_\mu(\mathbf{r})\, \mathrm{d}^3\mathrm{r}$. (4) Fourier transform $\Delta\pi(t)$ and $\Delta F_\mu(t)$ (Eq. (2.5)) to $\Delta\tilde{\pi}(\omega)$ and $\Delta\tilde{F}_\mu(\omega)$. For sufficiently long time signals, the peaks in the spectra are well resolved, Gaussian shaped near an excitation frequency. This allows the determination of the excitation energy ω_{0n} in a manner that Eq. (2.8) yields a purely *real* quantity obtaining the corresponding NAC τ_{n0}^μ.

3. Applications to equilateral $H + H_2$

We apply the method to the $\mathrm{H} + \mathrm{H}_2$ system, using the adiabatic local density approximation (ALDA) [30] within the TDDFT approach. Our calculation is performed using a plane waves basis and Troullier–Martins norm conserving pseudopotentials for the H-atoms [31]. A local spin-density functional with the correlation functional of Perdew and Wang [32] was used. Time propagation method is the Chebyshev collocation approach developed recently [28,33]. The values of all parameters of the calculation are summarized in Table 1.

The results are compared with previously published work [3,34,35]. In Fig. 1 we present the results of two in-plane components of the NACs on the second atom for fixed hyper-spherical coordinates $\rho = 2.5\ a_0$ and $\phi = 120°$, as a function of θ (here, we refer the reader to [3] for explanation of the coordinates nomenclature). For $\theta > 1$ the agreement between the two calculations is quantitatively good. The energetics is also very close. However, as the conical intersection is approached further, agreement quickly degrades. This is seen first also when considering the adiabatic potential energy curve on the same path in Fig. 2. We could not find a true crossing within the ALDA calcu-

Table 1
Parameters of the calculations and their values

Parameter	Definition	Symbol	Value
Grid length		L	16 a_o
Grid spacing		Δx	0.5 a_o
H_a–H_b distance	(Fig. 3)	R	1.4 a_o
Path angle	(Fig. 3)	ξ	1°
Hyper-radius		ρ	2.5 a_o
Hyper-angle		ϕ	120°
Pulse duration	Eq. (2.2)	T	7 a.u.
Pulse center	Eq. (2.2)	T_0	20 a.u.
Pulse strength	Eq. (2.1)	η	1×10^{-5} a.u.
Fourier-window	Eq. (2.5)	σ	1×10^{3} a.u.

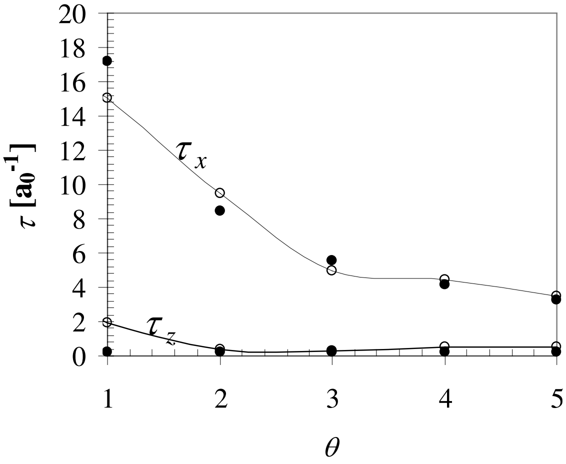

Fig. 1. The Cartesian components of the NACs on the second atom as a function of the hyper-spherical angle θ, computed using TDDFT (empty circles) and by Abrol et al. [3] (filled circles). The agreement is good for $\theta > 1$. For $\theta < 1$ (not shown) ALDA rapidly looses accuracy.

lation. This could be a result of the well known inadequacy of ALDA to describe near degeneracies.

Next, we compare with the DMBE results[35] along the path depicted in Fig. 3. The TDDFT z-Cartesian component of the NACs are shown in Fig. 4 along with those calculated by the DMBE method [35]. The two sets of results are in qualitative agreement. However, the present results decay considerably slower while receding from the CI and they are less peaked near the CI. The slow decay is a deficiency of the DMBE method, as indicated by Abrol et al. [3]. Yet the disagreement

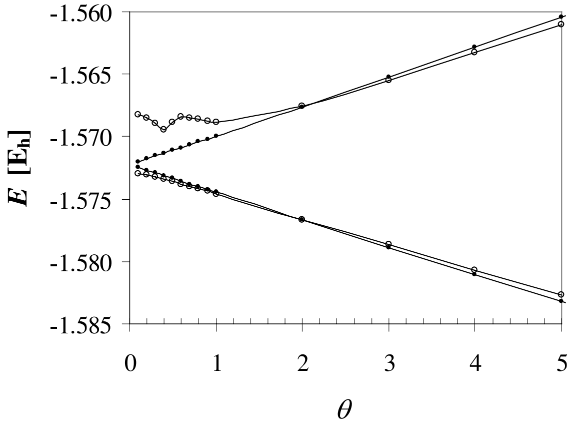

Fig. 2. The two adiabatic potential energy curves, as a function of the hyper-spherical angle θ, computed by DFT/TDDFT (empty circles) and by Abrol et al. [3] (filled circles). For $\theta > 1$ the agreement is very good. However, as the CI is approached even closer the ALDA results fail to show the crossing.

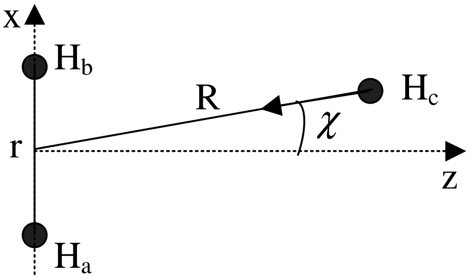

Fig. 3. The setup of the H + H_2 system. See text for details.

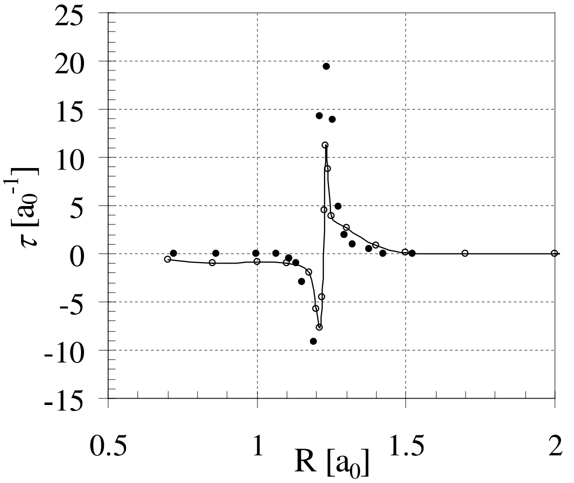

Fig. 4. The z component of the NAC along the path depicted in Fig. 3. Superimposed, as filled circles, the DMBE results [35].

close to the CI is again an indication that ALDA is inadequate near the CI.

We conclude from these results that the NACs can be calculated to good accuracy as long as the conical intersection is not approached too closely. It is not yet clear why the ALDA results degrade near the conical intersection. It is known however that LDA and ALDA cannot always handle near degeneracies well and this may certainly be the problem. Further work needs to be invested in order to study this problem.

4. Summary

A method was developed to compute the NACs between the ground and excited states from time-dependent density functional theory, formulated in real time. We have tested the method on the conical intersection of the reactive H_3 system, using the adiabatic local density approximation. We compared our results with those of Abrol et al. [3] and those of Varandas et al. [3]. We find that as long as the conical intersection is not too closely approached, the NACs are well characterized by ALDA. Closer to the degeneracy the calculation of the energy separation, as well as the NACs fail. The reason for this is probably the known inadequacy of LDA and ALDA near electronic degeneracies.

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