

Non-adiabatic couplings in density-functional theory for ensembles

Emmanuel Fromager

Laboratoire de Chimie Quantique, Université de Strasbourg, France

fromagere@unistra.fr

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Molecular Schrödinger equation

- In order to model chemical problems in quantum mechanics we should in principle solve the *molecular Schrödinger equation*.
- "molecular" means *electronic and nuclear*.
- For clarity, we will consider a *diatomic* molecule $A-B$ (without loss of generality) and denote $R = R_{AB}$ the *bond distance*.
- Rotation will be ignored.
- The molecular wavefunction $\Psi^{\text{mol}}(R, \mathbf{q})$ depends not only on the *electronic* space (and spin) *coordinates* $\mathbf{q} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ but *also* on the *bond distance* R .
- Finally, we assume that the mass M of nucleus B is much larger than the mass m of nucleus A ($m \ll M$) thus leading to the following Schrödinger equation for the molecule

$$\hat{H}^{\text{mol}}\Psi^{\text{mol}}(R, \mathbf{q}) = E^{\text{mol}}\Psi^{\text{mol}}(R, \mathbf{q})$$

where the molecular Hamiltonian equals in atomic units

$$\hat{H}^{\text{mol}} \equiv -\frac{1}{2m} \frac{\partial^2}{\partial R^2} + \frac{Z_A Z_B}{R} + \hat{H}(R)$$

- The *N -electron Hamiltonian* $\hat{H}(R)$, which is *geometry-dependent*, reads

$$\hat{H}(R) \equiv -\frac{1}{2} \sum_{i=1}^N \nabla_{\mathbf{r}_i}^2 - \sum_{i=1}^N \left(\frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \frac{Z_B}{|\mathbf{r}_i - \mathbf{R}_B|} \right) + \sum_{i < j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Molecular wavefunction

- We will show that the molecular wavefunction can be expressed exactly in terms of nuclear and electronic (ground- and excited-state) wavefunctions.
- Let us consider, for a *fixed* bond distance R , the solutions $\left\{ \Psi_I(R, \mathbf{q}) = \langle \mathbf{q} | \Psi_I(R) \rangle \right\}_{I=0,1,\dots}$ to the *electronic Schrödinger equation*

$$\hat{H}(R) |\Psi_I(R)\rangle = E_I(R) |\Psi_I(R)\rangle$$

- For *any* bond distance R , the electronic resolution of the identity formula holds:

$$|\mathbf{q}\rangle = \sum_I |\Psi_I(R)\rangle \langle \Psi_I(R) | \mathbf{q} \rangle = \sum_I \Psi_I^*(R, \mathbf{q}) |\Psi_I(R)\rangle$$

- Since $\Psi^{\text{mol}}(R, \mathbf{q}) = \langle R, \mathbf{q} | \Psi^{\text{mol}} \rangle$ with $|R, \mathbf{q}\rangle = |R\rangle \otimes |\mathbf{q}\rangle = \sum_I \Psi_I^*(R, \mathbf{q}) |R, \Psi_I(R)\rangle$

we finally obtain the *exact decomposition*

$$\Psi^{\text{mol}}(R, \mathbf{q}) = \sum_I \Psi_I(R, \mathbf{q}) \chi^I(R)$$

where the (to-be-determined) *I*th *nuclear wavefunction* reads $\chi^I(R) = \langle R, \Psi_I(R) | \Psi^{\text{mol}} \rangle$.

Born–Oppenheimer and adiabatic approximations

- In the so-called *Born-Oppenheimer approximation*, nuclear wavefunctions are determined from a *single* (ground or excited) electronic state:

$$\sum_I \Psi_I(R, \mathbf{q}) \chi^I(R) \rightarrow \Psi_{I_0}(R, \mathbf{q}) \chi^{I_0}(R)$$

- Within the so-called *adiabatic approximation*, variations of the electronic wavefunction with nuclear displacements are neglected: $\partial \Psi_{I_0}(R, \mathbf{q}) / \partial R \approx 0 \approx \partial^2 \Psi_{I_0}(R, \mathbf{q}) / \partial R^2$.
- Such an approximation is in principle relevant when the molecule is at *equilibrium* (R does not vary significantly).
- In this case, the nuclear wavefunction fulfills the following Schrödinger equation

$$\left[-\frac{1}{2m} \frac{d^2}{dR^2} + V_{I_0}(R) \right] \chi_n^{I_0}(R) = E_n^{\text{mol}} \chi_n^{I_0}(R),$$

where

$$V_{I_0}(R) = E_{I_0}(R) + \frac{Z_A Z_B}{R}.$$

- $V_{I_0}(R)$ is the potential interaction energy between the two nuclei *in the field of electrons* that are described by the wavefunction $\Psi_{I_0}(R, \mathbf{q})$.

Harmonic approximation

- Let us consider *fluctuations* $x = R - R_0$ around the equilibrium bond distance R_0 .
- From the Taylor expansion through second order in x ,

$$V_{l_0}(R) = V_{l_0}(R_0 + x) \approx V_{l_0}(R_0) + \frac{1}{2} \left(\frac{d^2 V_{l_0}(R)}{dR^2} \Big|_{R=R_0} \right) x^2,$$

we recover the Schrödinger equation for the **harmonic oscillator** with frequency

$$\omega_{l_0} = \sqrt{\frac{1}{m} \frac{d^2 V_{l_0}(R)}{dR^2} \Big|_{R=R_0}} \quad \text{or, equivalently, with constant } k_{l_0} = \frac{d^2 V_{l_0}(R)}{dR^2} \Big|_{R=R_0},$$

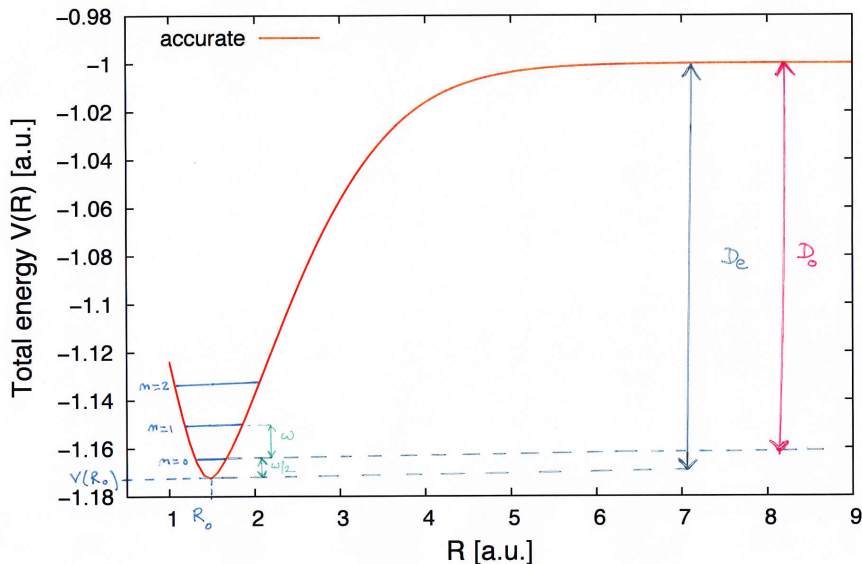
$$\left[-\frac{1}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega_{l_0}^2 x^2 \right] \varphi_n^{l_0}(x) = \left(E_n^{\text{mol}} - V_{l_0}(R_0) \right) \varphi_n^{l_0}(x)$$

where $\varphi_n^{l_0}(x) = \chi_n^{l_0}(R_0 + x)$.

- This approximation is known as the *harmonic approximation*.

Harmonic approximation

H₂



Non-adiabatic couplings

- Let us return to the *exact theory* and insert the decomposition $\Psi^{\text{mol}}(R, \mathbf{q}) = \sum_I \Psi_I(R, \mathbf{q}) \chi^I(R)$ into the molecular Schrödinger equation, thus leading to

$$-\frac{1}{2m} \sum_I \left[\Psi_I(R, \mathbf{q}) \frac{d^2 \chi^I(R)}{dR^2} + 2 \frac{\partial \Psi_I(R, \mathbf{q})}{\partial R} \frac{d \chi^I(R)}{dR} + \frac{\partial^2 \Psi_I(R, \mathbf{q})}{\partial R^2} \chi^I(R) \right] + \sum_I \left[\frac{Z_A Z_B}{R} + E_I(R) \right] \Psi_I(R, \mathbf{q}) \chi^I(R) = E^{\text{mol}} \sum_I \Psi_I(R, \mathbf{q}) \chi^I(R).$$

- From the orthonormalization condition $\langle \Psi_J(R) | \Psi_I(R) \rangle = \int d\mathbf{q} \Psi_J^*(R, \mathbf{q}) \Psi_I(R, \mathbf{q}) = \delta_{IJ}$, we finally obtain *coupled* Schrödinger equations for the nuclear wavefunctions,

$$\left[-\frac{1}{2m} \frac{d^2}{dR^2} + \frac{Z_A Z_B}{R} + E_J(R) \right] \chi^J(R) - \frac{1}{2m} \sum_I \left[2F_{JI}(R) \frac{d}{dR} + G_{JI}(R) \right] \chi^I(R) = E^{\text{mol}} \chi^J(R)$$

where the so-called *non adiabatic couplings* (NACs) read

$$F_{JI}(R) = \left\langle \Psi_J(R) \left| \frac{d\Psi_I(R)}{dR} \right. \right\rangle \quad \text{and} \quad G_{JI}(R) = \left\langle \Psi_J(R) \left| \frac{d^2 \Psi_I(R)}{dR^2} \right. \right\rangle.$$

Non-adiabatic couplings in ensemble DFT

- Note that $F_{JI}(R) = -F_{IJ}^*(R)$ since $\frac{d}{dR} \left[\langle \Psi_J(R) | \Psi_I(R) \rangle \right] = \frac{d\delta_{IJ}}{dR} = 0$.
- As a result, for *real* electronic wavefunctions, $F_{II}(R) = 0$.
- NACs can be connected to *electronic energies* as follows,

$$\langle \Psi_J(R) | \hat{H}(R) | \Psi_I(R) \rangle = \delta_{IJ} E_I(R) \xrightarrow{\frac{d}{dR}} F_{JI}(R) = \frac{\left\langle \Psi_J(R) \left| \frac{\partial \hat{H}(R)}{\partial R} \right| \Psi_I(R) \right\rangle - \delta_{IJ} \frac{dE_I(R)}{dR}}{E_I(R) - E_J(R)}$$

- Similarly, NACs can be determined for a *fictitious* Kohn–Sham (KS) system whose (ensemble) density equals the true physical one:

$$F_{JI}^{\text{KS}}(R) = \frac{\left\langle \Phi_J^{\text{KS}}(R) \left| \frac{\partial \hat{H}^{\text{KS}}(R)}{\partial R} \right| \Phi_I^{\text{KS}}(R) \right\rangle - \delta_{IJ} \frac{d\mathcal{E}_I^{\text{KS}}(R)}{dR}}{\mathcal{E}_I^{\text{KS}}(R) - \mathcal{E}_J^{\text{KS}}(R)}$$

Non-adiabatic couplings in ensemble DFT

- There is *a priori* no reason for the KS NACs to be equal to the true physical ones.
- Nevertheless, we know from ensemble DFT that *KS and physical energy differences can be connected* as follows,

$$E_I(R) - E_J(R) = \mathcal{E}_I^{\text{KS}}(R) - \mathcal{E}_J^{\text{KS}}(R) + \sum_{K>0} (\delta_{KI} - \delta_{KJ}) \left. \frac{\partial E_{\text{Hxc}}^w[n]}{\partial w_K} \right|_{n=n^w(R)}$$

where the (geometry-dependent) ensemble density reads

$$\begin{aligned} n^w(R) &= n_{\psi_0(R)} + \sum_{K>0} w_K (n_{\psi_K(R)} - n_{\psi_0(R)}) \\ &= n_{\phi_0^{\text{KS}}(R)} + \sum_{K>0} w_K (n_{\phi_K^{\text{KS}}(R)} - n_{\phi_0^{\text{KS}}(R)}) \end{aligned}$$

- Consequently, we obtain the following exact relation (for $I \neq J$),

$$\frac{\left\langle \psi_J(R) \left| \frac{\partial \hat{H}(R)}{\partial R} \right| \psi_I(R) \right\rangle}{F_{JI}(R)} = \frac{\left\langle \phi_J^{\text{KS}}(R) \left| \frac{\partial \hat{H}^{\text{KS}}(R)}{\partial R} \right| \phi_I^{\text{KS}}(R) \right\rangle}{F_{JI}^{\text{KS}}(R)} + \sum_{K>0} (\delta_{KI} - \delta_{KJ}) \left. \frac{\partial E_{\text{Hxc}}^w[n]}{\partial w_K} \right|_{n=n^w(R)}$$

Non-adiabatic couplings in DFT

- Note that the Hxc *kernel* (which is a key quantity in time-dependent DFT) appears in the following contribution,

$$\frac{\partial \hat{H}^{\text{KS}}(R)}{\partial R} = \frac{\partial \hat{H}(R)}{\partial R} + \sum_{i=1}^N \int d\mathbf{r} \frac{\delta^2 E_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}(R)]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}_i)} \frac{\partial n^{\mathbf{w}}(R, \mathbf{r})}{\partial R} \times$$

- How can we turn these derivations into a *practical method* for computing NACs ?
- If, for convenience, we *approximate the physical wavefunctions with the KS ones* then

$$F_{JI}(R) \approx \frac{\left\langle \Phi_J^{\text{KS}}(R) \left| \frac{\partial \hat{H}(R)}{\partial R} \right| \Phi_I^{\text{KS}}(R) \right\rangle}{\mathcal{E}_I^{\text{KS}}(R) - \mathcal{E}_J^{\text{KS}}(R) + \sum_{K>0} (\delta_{KI} - \delta_{KJ}) \left. \frac{\partial E_{\text{Hxc}}^{\mathbf{w}}[n]}{\partial w_K} \right|_{n=n^{\mathbf{w}}(R)}}$$

- The latter approximation should be tested on the Hubbard dimer !