

Comment on “Nonadiabatic couplings from the Kohn-Sham derivative matrix: Formulation by time-dependent density-functional theory and evaluation in the pseudopotential framework”

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The issue of the *ab initio* evaluation of the first-order nonadiabatic couplings (NAC's) is re-examined. In particular, a recent derivation in [Phys. Rev. A **82**, 062508 \(2010\)](#) of the NAC's is corrected by performing an extension of the derivation to the case of arbitrary values of the Kohn-Sham (KS) occupation factors. A single expression for the nonadiabatic couplings, valid both for integer and fractional values of the KS occupation factors, is provided.

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This Comment is aimed to correct and extend some results derived in Ref. [1], concerning the important issue of the *ab initio* calculation of the first-order nonadiabatic couplings (NAC's) [2–6], in the context of the Born treatment of the coupled electrons-nuclei problem [7].

Following the notation in Refs. [1] and [6], the NAC's between the ground and excited electronic states are defined as

$$\langle \Psi_0 | \frac{\partial}{\partial R_\mu} | \Psi_I \rangle = \omega_I^{-1} \langle \Psi_0 | \frac{\partial \hat{H}}{\partial R_\mu} | \Psi_I \rangle = \omega_I^{-3/2} \mathbf{h}_\mu^\dagger \mathbf{S}^{-1/2} \mathbf{F}_I. \quad (1)$$

Here, Ψ_0 (Ψ_I) is the many-body electronic wave function of the ground (I th excited state). R_μ is the nuclear coordinate with μ representing x , y , z components and the atom index, \hat{H} is the many-body Hamiltonian, and ω_I (>0) is the ground- \rightarrow excited-state excitation energy. Components of \mathbf{h}_μ and matrix elements of \mathbf{S} are given by

$$\begin{aligned} (\mathbf{h}_\mu)_{ij\sigma} &:= h_{\mu,ij\sigma} = \langle \psi_{i\sigma} | \partial \hat{H} / \partial R_\mu | \psi_{j\sigma} \rangle, \\ &= \langle \psi_{i\sigma} | \partial \hat{V}^{\text{en}} / \partial R_\mu | \psi_{j\sigma} \rangle, \end{aligned} \quad (2)$$

and

$$S_{ij\sigma,kl\tau} = \frac{\delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l}}{(f_{i\sigma} - f_{j\sigma})(\varepsilon_{j\sigma} - \varepsilon_{i\sigma})} = \frac{\delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l}}{\Delta f_{ij\sigma} \Delta \varepsilon_{ji\sigma}}, \quad (3)$$

where $\psi_{i\sigma}$, $\varepsilon_{i\sigma}$, and $f_{i\sigma}$ are the electronic wave function, eigenvalue, and occupation number for the single-particle i th Kohn-Sham (KS) auxiliary state with spin σ , and $\Delta f_{ij\sigma} = f_{i\sigma} - f_{j\sigma}$, $\Delta \varepsilon_{ji\sigma} = \varepsilon_{j\sigma} - \varepsilon_{i\sigma}$. \hat{V}^{en} is the potential from the nuclear charge. It is important to note that if $\varepsilon_{i\sigma} < \varepsilon_{j\sigma} \leftrightarrow f_{i\sigma} > f_{j\sigma}$, then $\Delta f_{ij\sigma} \Delta \varepsilon_{ji\sigma} > 0 \rightarrow S_{ij\sigma,kl\tau} > 0$. \mathbf{F}_I is the eigenvector of the Casida equations [8]

$$\Omega \mathbf{F}_I = \omega_I^2 \mathbf{F}_I, \quad (4)$$

where

$$\begin{aligned} \Omega_{ij\sigma,kl\tau} &= \delta_{\sigma,\tau} \delta_{i,k} \delta_{j,l} \Delta \varepsilon_{ij\sigma} \Delta \varepsilon_{kl\tau} \\ &+ 2 \sqrt{\Delta f_{ij\sigma} \Delta \varepsilon_{ji\sigma}} K_{ij\sigma,kl\tau} \sqrt{\Delta f_{kl\tau} \Delta \varepsilon_{lk\tau}}, \end{aligned} \quad (5)$$

with \mathbf{K} being the KS matrix of the Hartree (H) and exchange-correlation (xc) kernel Λ^{Hxc} ,

$$\begin{aligned} K_{ij\sigma,kl\tau} &= \int d^3r \int d^3r' \psi_{i\sigma}(\mathbf{r}) \psi_{j\sigma}(\mathbf{r}) \Lambda^{\text{Hxc}}(\mathbf{r}, \mathbf{r}') \psi_{k\tau}(\mathbf{r}') \psi_{l\tau}(\mathbf{r}'). \end{aligned} \quad (6)$$

The kernel $\Lambda^{\text{Hxc}}(\mathbf{r}, \mathbf{r}')$ may be obtained from straightforward application of density-functional perturbation theory (DFPT) [9], as shown in Ref. [6]. The set of Eqs. (1)–(6) defines the so-called “ h representation” of the NAC's. It has the virtue that the NAC's as given and defined in a many-body framework by the left-hand side (lhs) of Eq. (1) can be evaluated by using quantities that may be obtained from linear-response time-dependent DFT (LR-TDDFT) [10] [right-hand side (rhs) of Eq. (1)]. For systems with a large number of electrons, the computational cost of evaluating the rhs of Eq. (1) is much lower than the lhs.

As a way to solve technical problems related to the practical evaluation of the rhs of Eq. (1) in a pseudopotential numerical framework, in Ref. [1] the so-called “ d representation” of the NAC's has been introduced, according to which one has

$$\langle \Psi_0 | \frac{\partial}{\partial R_\mu} | \Psi_I \rangle = \omega_I^{1/2} \mathbf{d}_\mu^\dagger \mathbf{S}^{1/2} \mathbf{F}_I, \quad (7)$$

instead of Eq. (1). Here,

$$\begin{aligned} (\mathbf{d}_\mu)_{ij\sigma} &:= d_{\mu,ij\sigma} = \frac{\langle \psi_{i\sigma} | \partial \hat{H}^{\text{KS}} / \partial R_\mu | \psi_{j\sigma} \rangle}{\Delta \varepsilon_{ji\sigma}}, \\ &= \frac{\langle \psi_{i\sigma} | \partial \hat{V}^{\text{eff}} / \partial R_\mu | \psi_{j\sigma} \rangle}{\Delta \varepsilon_{ji\sigma}}, \end{aligned}$$

where \hat{H}^{KS} is the Kohn-Sham Hamiltonian, and \hat{V}^{eff} is the corresponding KS effective potential. Inserting Eq. (3) in Eq. (7), one obtains the explicit expression

$$\langle \Psi_0 | \frac{\partial}{\partial R_\mu} | \Psi_I \rangle = \omega_I^{1/2} \sum_{i,j,\sigma}^{\Delta f_{ij\sigma} > 0} \frac{(\mathbf{d}_\mu^\dagger)_{ij\sigma} (\mathbf{F}_I)_{ij\sigma}}{\sqrt{\Delta f_{ij\sigma} \Delta \varepsilon_{ji\sigma}}}. \quad (8)$$

Equation (7) [or Eq. (8)] is the main result of Ref. [1], and in the remaining part of this Comment its correctness will be disputed.

The crucial step in obtaining Eq. (7) is the derivation of the relationship $\mathbf{F}_I^\dagger \mathbf{S}^{-1/2} \mathbf{h}_\mu = \mathbf{F}_I^\dagger \Omega \mathbf{S}^{1/2} \mathbf{d}_\mu$, that is achieved in Eq. (17) of Ref. [1], in several steps. Since this equation is

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the source of the problem in Eq. (7), the derivation of this relationship will be repeated here,

$$\begin{aligned} \mathbf{F}_I^\dagger \mathbf{S}^{-1/2} \mathbf{h}_\mu &= \sum_{i,j,\sigma}^{\Delta f_{ij\sigma} > 0} (\mathbf{F}_I^\dagger)_{ij\sigma} \sqrt{\Delta f_{ij\sigma} \Delta \varepsilon_{ji\sigma}} h_{\mu,ij\sigma}, \\ &= \sum_{i,j,\sigma}^{\Delta f_{ij\sigma} > 0} \sum_{k,l,\tau}^{\Delta f_{kl\tau} > 0} (\mathbf{F}_I^\dagger)_{ij\sigma} \Omega_{ij\sigma,kl\tau} \sqrt{\frac{\Delta f_{kl\tau}}{\Delta \varepsilon_{lk\tau}}} d_{\mu,kl\tau}, \\ &= \mathbf{F}_I^\dagger \boldsymbol{\Omega} \mathbf{S}^{-1/2} \mathbf{D}_\mu. \end{aligned} \quad (9)$$

Here, $D_{\mu,ij\sigma} = d_{\mu,ij\sigma} / \Delta \varepsilon_{ji\sigma}$, and in consequence the correct fundamental link between the “ h representation” and the “ d representation” is given by

$$\mathbf{h}_\mu = \mathbf{S}^{1/2} \boldsymbol{\Omega} \mathbf{S}^{-1/2} \mathbf{D}_\mu. \quad (10)$$

Replacing Eq. (10) in Eq. (1), one obtains for the NACs

$$\langle \Psi_0 | \frac{\partial}{\partial R_\mu} | \Psi_I \rangle = \omega_I^{1/2} \mathbf{D}_\mu^\dagger \mathbf{S}^{-1/2} \mathbf{F}_I, \quad (11)$$

which is different from the result in Ref. [1], as given in Eq. (7). The difference between Eqs. (7) and (11) may be made more explicit by inserting Eq. (3) in equation above, obtaining

$$\langle \Psi_0 | \frac{\partial}{\partial R_\mu} | \Psi_I \rangle = \omega_I^{1/2} \sum_{i,j,\sigma}^{\Delta f_{ij\sigma} > 0} (\mathbf{d}_\mu^\dagger)_{ij\sigma} \sqrt{\frac{\Delta f_{ij\sigma}}{\Delta \varepsilon_{ji\sigma}}} (\mathbf{F}_I)_{ij\sigma}. \quad (12)$$

For *fractional* values of the occupation numbers ($f_{i\sigma} \neq 1$, $f_{j\sigma} \neq 0$), Eqs. (8) and (12) are fundamentally different, with the difference being particularly important for the quasiequal occupancy situation $f_{i\sigma} \cong f_{j\sigma}$. It should be emphasized that the d representation of the NAC’s as given in Eq. (11) is valid *both* for fractional and integer values of the occupation factors. Beyond its practical value for the evaluation of the NAC’s in open-shell situations (just to give an example), it provides a unified and consistent treatment of both situations, with the integer occupation case being just a particular case of the general situation with fractional occupation factors. The present results suggest also a reconsideration of the application

of the Slater transition method for NAC’s in doublet systems, where equal occupancies ($=1/2$) are usually assumed for the electron-hole pair in the midexcited state [1,11]. It should be emphasized that the *only* way to arrive at the correct expression for the NAC’s as given by Eq. (11) is by keeping the explicit dependence on the occupation factors until the end of the calculation (as made above), and only then take the integer occupation limit $\Delta f_{ij\sigma} = 1$ if needed.

The difference between Eqs. (8) and (12) [or between Eqs. (7) and (11)], comes from the dependence on the occupation factors: $(\Delta f_{ij\sigma})^{1/2}$ appears in the denominator of Eq. (8), but it appears in the numerator of Eq. (12). The two expressions become the same only under the *ad hoc* assumption that $\Delta f_{ij\sigma} = 1$, that seems to be the path followed by the authors of Ref. [1] for the derivation of Eq. (7). The situation is at least confusing regarding this issue, as in their recent publication on the same topic (Ref. [6]), they quote again the same result for the NAC’s in the d representation [Eq. (12) in Ref. [6]], without giving any warning on the possible (or assumed) values for the occupation numbers. Furthermore, it should be pointed out that there is a typing error in the third line of Eq. (17) of Ref. [1]: The product of three Kronecker δ functions should not exist and must be removed. Only after this removal and the commented assumption on the occupations number configuration is the final expression of Eq. (17) in Ref. [1] correct.

Equation (11) (and its associated derivation) is the main result of this Comment, and it corrects the result of Eq. (7). They are equivalent only for the particular case of integer values of the occupation factors. Equation (11) is the correct expression for the NAC’s both for integer and fractional values of the occupation factors. Based on this, it is suggested to use the rigorous Eq. (11) for the *ab initio* evaluation of the nonadiabatic couplings, instead of the approximated Eq. (7), as has been done so far.

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