Derivation of nonadiabatic couplings and the Born-Oppenheimer Approximation

Ansatz for the total (electronic-nuclear) wave function: $\Psi(r,R,t) = \sum_{l=0}^{\infty} \Phi_l(r,R)\,\chi_l(R,t)$

where Φ_l's are solutions of the time-independent electronic Schrödinger equation:

$$\hat{H}^{ele}_{(r,R)}\,\Phi_l(r,R) = E_l\,\Phi_l(r,R)$$

→ time-dependent electronic-nuclear Schrödinger equation: $i\hbar \frac{\partial \Psi(r,R,t)}{\partial t} = \hat{H}(r,R)\,\Psi(r,R,t)$

$$\hat{H}(r,R) = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + \hat{H}^{ele}(r,$$

$$\underbrace{i\hbar \frac{\partial}{\partial t}\left(\sum_{l=0}^{\infty}\Phi_l(r,R)\,\chi_l(R,t)\right)}_{= i\hbar \sum_{l=0}^{\infty}\Phi_l(r,R)\frac{\partial \chi_l(R,t)}{\partial t}} = \Bigg[\underbrace{-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\left(\sum_{l=0}^{\infty}\Phi_l(r,R)\,\chi_l(R,t)\right)} + \underbrace{\hat{H}^{ele}(r,R)\left(\sum_{l=0}^{\infty}\Phi_l(r,R)\,\chi_l(R,t)\right)}_{= \sum_{l=0}^{\infty} E_l(R)\,\Phi_l(r,R)\,\chi_l(R,t)}$$

$$-\sum_I \frac{\hbar^2}{2M_I}\nabla_I\left[\nabla_I \sum_{l=0}^{\infty}\Phi_l(r,R)\,\chi_l(R,t)\right] = \sum_{l=0}^{\infty} -\sum_I \frac{\hbar^2}{2M_I}\nabla_I\left[\left(\nabla_I\Phi_l(r,R)\right)\chi_l(R,t) + \Phi_l(r,R)\,\nabla_I\chi_l(R,t)\right]$$

$$= \sum_{l=0}^{\infty} -\sum_I \frac{\hbar^2}{2M_I}\left[\left(\nabla_I^2\Phi_l(r,R)\right)\chi_l(R,t) + \left(\nabla_I\Phi_l(r,R)\right)\nabla_I\chi_l(R,t) + \left(\nabla_I\Phi_l(r,R)\right)\nabla_I\chi_l(R,t) + \Phi_l(r,R)\,\nabla_I^2\chi_l(R,t)\right.$$

$$i\hbar \sum_{l=0}^{\infty}\Phi_l(r,R)\frac{\partial \chi_l(R,t)}{\partial t} = \sum_{l=0}^{\infty}\left\{-\sum_I \frac{\hbar^2}{2M_I}\left[\left(\nabla_I^2\Phi_l(r,R)\right)\chi_l(R,t) + 2\left(\nabla_I\Phi_l(r,R)\right)\nabla_I\chi_l(R,t) + \Phi_l(r,R)\,\nabla_I^2\chi_l(R,t)\right] + E_l(R)\,\Phi_l\,\chi_l(\right.$$

⇒ multiply from left with $\Phi_k^*(r,R)$ and integrate over all electronic variables $\int dr$

$$i\hbar \sum_{l=0}^{\infty}\left[\int dr\, \Phi_k^*(r,R)\,\Phi_l(r,R)\,\frac{\partial \chi_l(R,t)}{\partial t}\right] = \sum_{l=0}\Bigg[\int dr\,\Phi_k^*(r,R)\,E_l(R)\,\Phi_l(r,R)\,\chi_l(R,t) - \sum_I \frac{\hbar^2}{2M_I}\Big\{\int dr\,\Phi_k^*(r,R)\left(\nabla_I^2\Phi_l(r,R)\right)\chi_l(R,t)$$

$$+\, 2\int dr\,\Phi_k^*(r,R)\left(\nabla_I\Phi_l(r,R)\right)\nabla_I\chi_l(R,t) + \int dr\,\Phi_k^*(r,R)\,\Phi_l(r,R)\,\nabla_I^2\chi_l(R,t)\Big\}\Bigg] \qquad (2$$

$$i\hbar\frac{\partial \chi_k(R,t)}{\partial t} = E_k(R)\,\chi_k(R,t) + \sum_{l=0}^{\infty}\left[-\sum_I\frac{\hbar^2}{2M_I}\left\{\int dr\,\Phi_k^*(r,R)\left(\nabla_I^2\Phi_l(r,R)\right)\chi_l(R,t) + 2\int dr\,\Phi_k^*(r,R)\left(\nabla_I\Phi_l(r,R)\right)\nabla_I\chi_l(R,t)\right\}\right]$$

$$+ - \sum_I\frac{\hbar^2}{2M_I}\nabla_I^2\chi_k(R,t)$$

$$i\hbar\frac{\partial \chi_k(R,t)}{\partial t} = E_k(R)\,\chi_k(R,t) - \sum_I\frac{\hbar^2}{2M_I}\nabla_I^2\chi_k(R,t) + \sum_{l=0}^{\infty} - \sum_I\frac{\hbar^2}{2M_I}\left[\int dr\,\Phi_k^*(r,R)\left(\nabla_I^2\Phi_l(r,R)\right)\chi_l(R,t) + 2\int dr\,\Phi_k^*(r,R)\,\nabla_I\Phi_l \times \nabla_I\chi_l(R,t)\right]$$

$$i\hbar\frac{\partial \chi_k(R,t)}{\partial t} = \left[-\sum_I\frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(R)\right]\chi_k(R,t) + \sum_{l=0}^{\infty}\Bigg\{\underbrace{\int dr\,\Phi_k^*(r,R)\left[-\sum_I\frac{\hbar^2}{2M_I}\nabla_I^2\right]\Phi_l(r,R)}_{\substack{\text{2nd order nonadiabatic} \\ \text{coupling elements} \\ D_{kl}}} + \sum_I\frac{1}{M_I}\overbrace{\int \Phi_k^*(r,R)\left(-i\hbar\nabla_I\right)\Phi_l}^{\substack{\text{1st order nonadiabatic} \\ \text{coupling vector}}} \times \left(-i\hbar\nabla_I\right.$$

$$\Rightarrow \boxed{i\hbar\frac{\partial \chi_k(R,t)}{\partial t} = \left[-\sum_I\frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(R)\right]\chi_k(R,t) - \sum_{l=0}^{\infty}\sum_I\left\{\frac{\hbar^2}{2M_I}D_{kl}^I + \frac{\hbar^2}{M_I}d_{kl}^I\right\}\chi_l(R,t)}$$

$$\boxed{i\hbar\frac{\partial \chi_k(R,t)}{\partial t} = \left[-\sum_I\frac{\hbar^2}{2M_I}\nabla_I^2 + E_k(R)\right]\chi_k(R,t) + \sum_{l=0}^{\infty} C_{kl}\,\chi_l(R,t)}$$

Derivation of Bohmian Dynamics

(adiabatic dynamics in one electronic state k

- nuclear wavefunction written in polar representation: $\chi_k(R,t) = A_k(R,t)\, e^{iS(R,t)/\hbar} \Rightarrow \chi = Ae^{iS/\hbar}$

↳ time-dependent nuclear Schrödinger equation: $\left[-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 + E\right]\chi = i\hbar\frac{\delta \chi}{\delta t}$

$$\Downarrow$$

$$-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2\left(Ae^{iS/\hbar}\right) + EAe^{iS/\hbar} = i\hbar\frac{\delta A}{\delta t}e^{iS/\hbar} + i\hbar A(i/\hbar)e^{iS/\hbar}\frac{\delta S}{\delta t}$$

$$-\sum_I \frac{\hbar^2}{2M_I}\nabla_I\left[(\nabla_I A)e^{iS/\hbar} + A(i/\hbar)e^{iS/\hbar}\nabla_I S\right] + EAe^{iS/\hbar} = i\hbar e^{iS/\hbar}\left(\frac{\delta A}{\delta t} + \frac{i}{\hbar}A\frac{\delta S}{\delta t}\right)$$

$$-\sum_I \frac{\hbar^2}{2M_I}\Big\{(\nabla_I^2 A)e^{iS/\hbar} + (\nabla_I A)(i/\hbar)e^{iS/\hbar}\nabla_I S + (\nabla_I A)(i/\hbar)e^{iS/\hbar}\nabla_I S + A(i/\hbar)(i/\hbar)e^{iS/\hbar}(\nabla_I S)(\nabla_I S) + A(i/\hbar)e^{iS/\hbar}\nabla_I^2 S\Big\}$$

$$\ldots + EAe^{iS/\hbar} = i\hbar e^{iS/\hbar}\left(\frac{\delta A}{\delta t} + \frac{i}{\hbar}A\frac{\delta S}{\delta t}\right)$$

$$-\cancel{e^{iS/\hbar}}\sum_I \frac{\hbar^2}{2M_I}\left[\nabla_I^2 A + \frac{2i}{\hbar}(\nabla_I A)(\nabla_I S) - \frac{1}{\hbar^2}A(\nabla_I S)^2 + \frac{i}{\hbar}A\nabla_I^2 S\right] + EA\cancel{e^{iS/\hbar}} = i\hbar\cancel{e^{iS/\hbar}}\left(\frac{\delta A}{\delta t} + \frac{i}{\hbar}A\frac{\delta S}{\delta t}\right)$$

$$\Rightarrow\quad -\sum_I \frac{\hbar^2}{2M_I}\left[\nabla_I^2 A + \frac{2i}{\hbar}(\nabla_I A)(\nabla_I S) - \frac{1}{\hbar^2}A(\nabla_I S)^2 + \frac{i}{\hbar}A\right] + EA = i\hbar\left(\frac{\delta A}{\delta t} + \frac{i}{\hbar}A\frac{\delta S}{\delta t}\right)$$

⇒ real part:

$$-\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 A + \sum_I \frac{1}{2M_I}A(\nabla_I S)^2 + EA = -A\frac{\delta S}{\delta t}$$

$$\Rightarrow\quad \boxed{\frac{\delta S}{\delta t} = \sum_I \frac{\hbar^2}{2M_I}\frac{\nabla_I^2 A}{A} - \sum_I \frac{1}{2M_I}(\nabla_I S)^2 - E}$$

⇒ imaginary part:

$$-\sum_I \frac{\cancel{\hbar}}{M_I}(\nabla_I A)(\nabla_I S) - \sum_I \frac{\cancel{\hbar}}{2M_I}A(\nabla_I^2 S) = \cancel{\hbar}\frac{\delta A}{\delta t} \Rightarrow \boxed{\frac{\delta A}{\delta t} = -\sum_I \frac{1}{M_I}(\nabla_I A)(\nabla_I S) - \sum_I \frac{1}{2M_I}A\nabla_I^2 S}$$