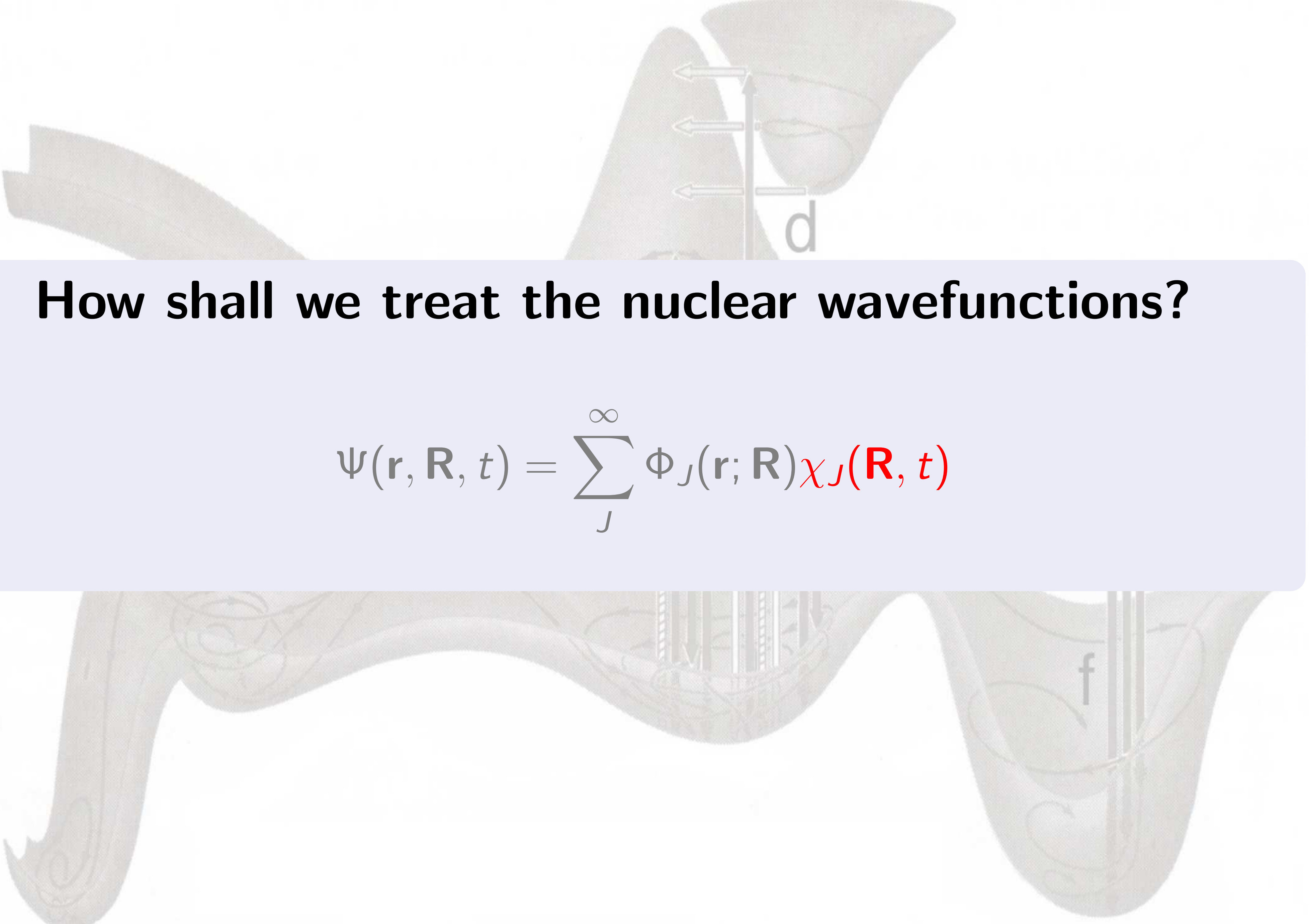
How shall we treat the nuclear wavefunctions?

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{J}^{\infty} \Phi_J(\mathbf{r}; \mathbf{R}) \chi_J(\mathbf{R}, t)$$

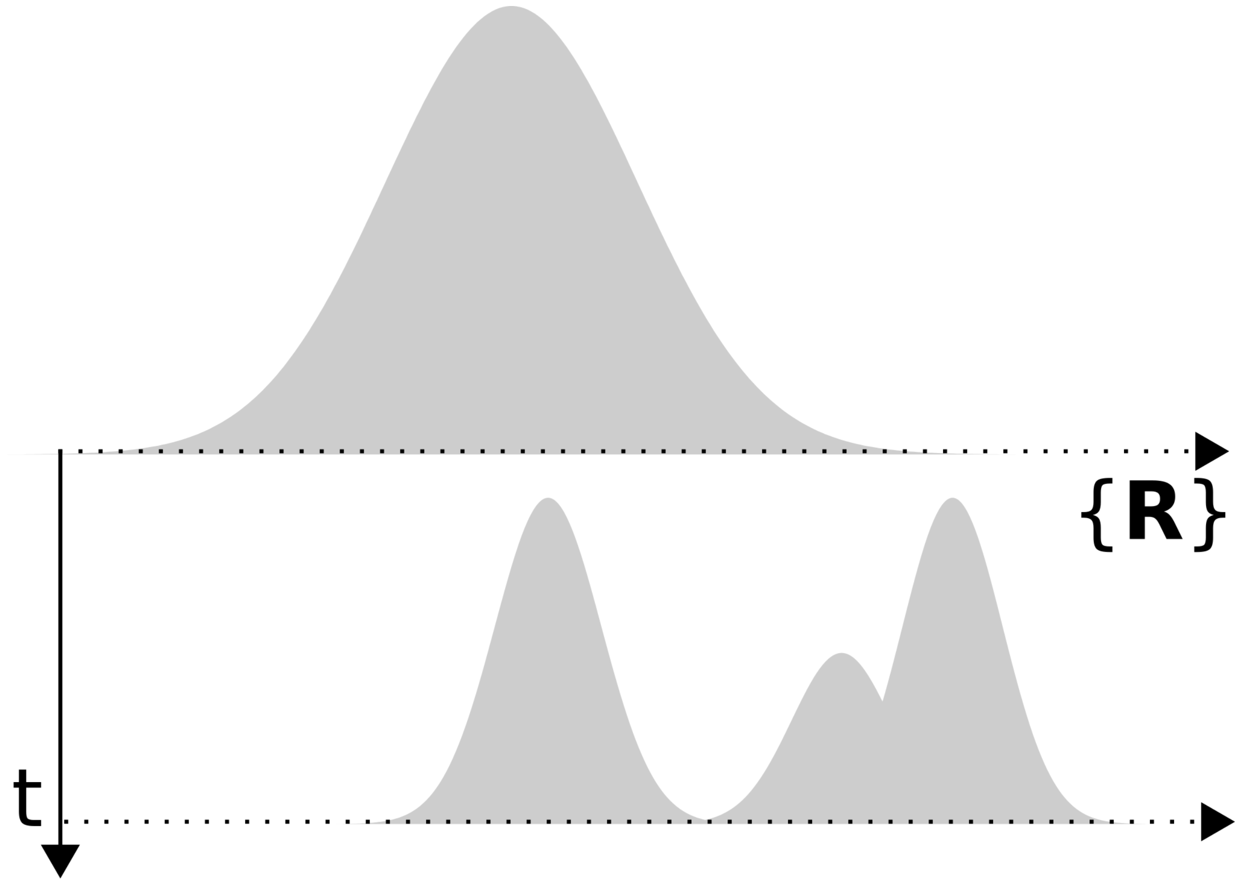


Credit: J. Michl and V. Bonacic-Koutecký, “Electronic Aspects of Organic Photochemistry”. John Wiley and Sons, Inc., New York, 1990.

Nuclear equations of motion

Nuclear wavefunction represented on a grid

$$\chi_I(R_1, ..., R_f, t) = \sum_{j_1}^{N_1} ... \sum_{j_f}^{N_f} C_{j_1 \dots j_f}(t) \prod_{\kappa}^{f} \chi_{j_k}^{(\kappa)}(R_\kappa)$$



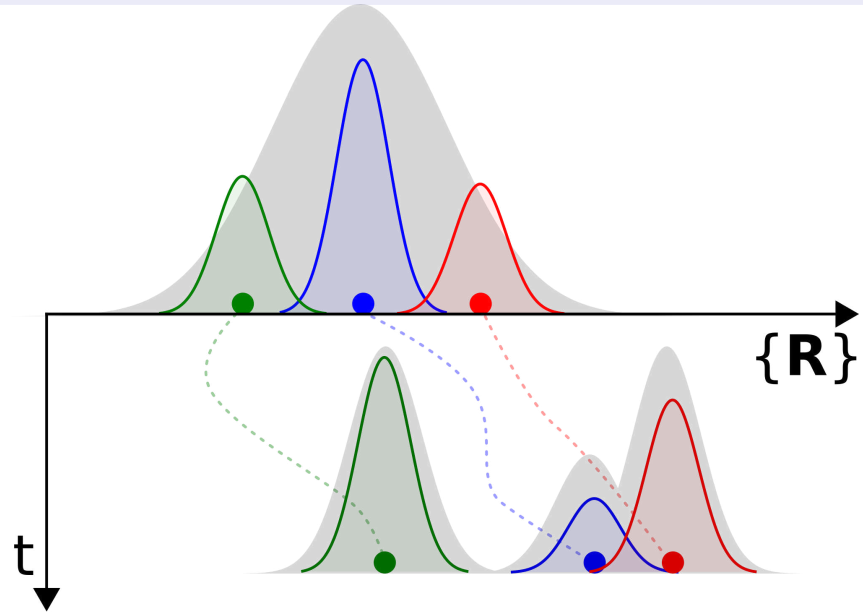
Multiconfiguration Time-Dependent Hartree (MCTDH)

G. A. Worth, H.-D. Meyer, H. Köppel, L. S. Cederbaum, I. Burghardt, *Int. Rev. Phys. Chem.*, **27**, 569 (2008).

Nonadiabatic quantum molecular dynamics

Nuclear wavefunction represented by trajectory basis functions (TBFs)

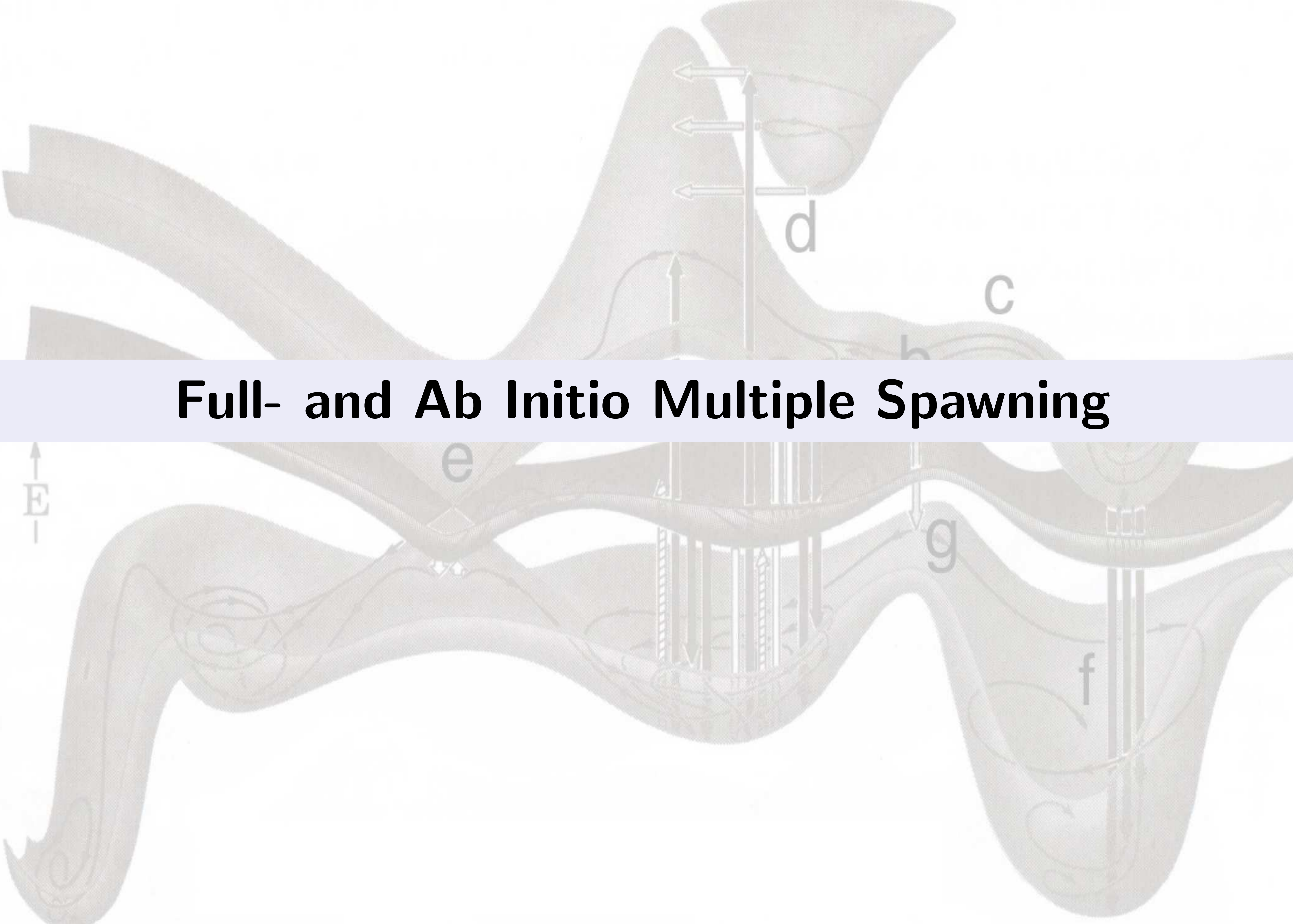
$$\chi_I(\mathbf{R},t) = \sum_k^{N_{TBFs}} C_k^I(t)\chi_k^I\left(\mathbf{R};\overline{\mathbf{R}}_k^I(t),\overline{\mathbf{P}}_k^I(t),\boldsymbol{\alpha}_k^I(t),\overline{\gamma}_k^I(t)\right)$$



variational MultiConfigurational Gaussian (vMCG) – Multiconfigurational Ehrenfest (MCE) – Ab Initio Multiple Cloning (AIMC) – Full Multiple Spawning (FMS)

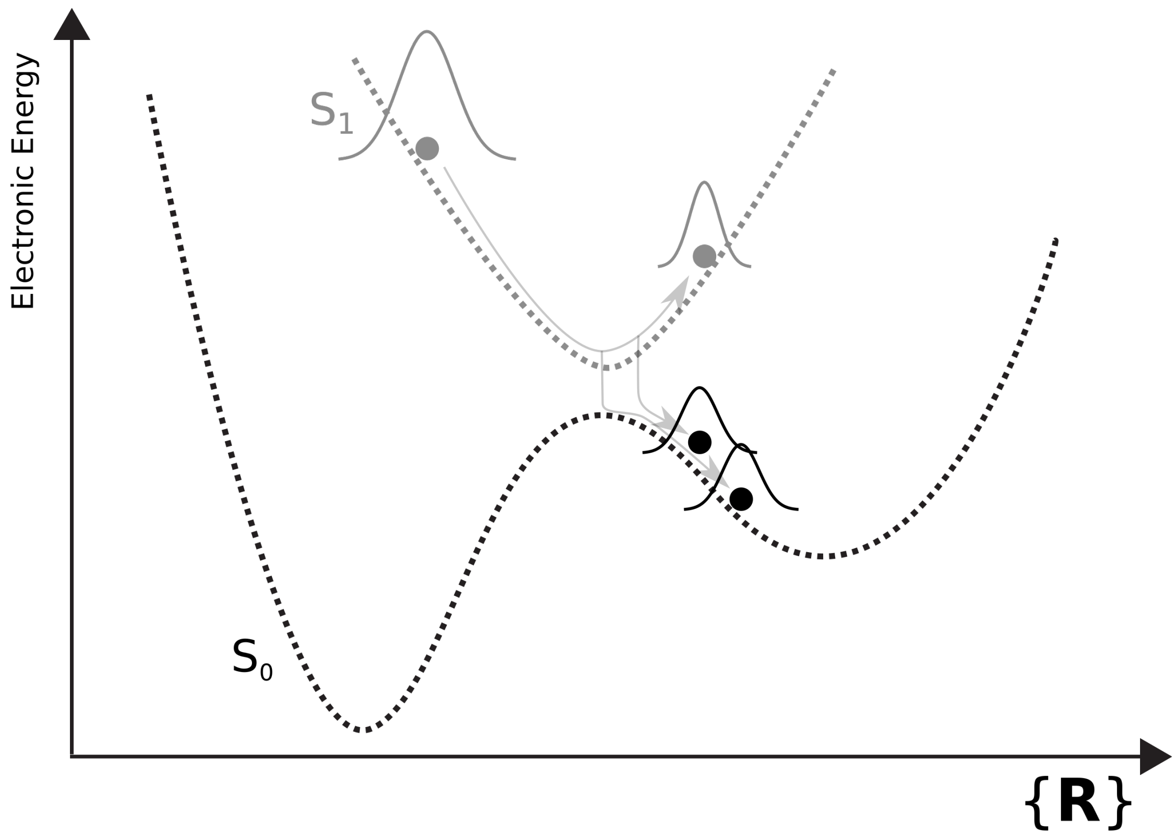
vMCG (Worth, Lasorne, Burghardt): *Faraday Discuss.*, **127**, 307 (2004); *Int. Rev. Phys. Chem.*, **34**, 269 (2015). **MCE** (Shalashilin): *J. Chem. Phys.*, **130**, 244101 (2009). **FMS** (Martínez): *J. Phys. Chem.*, **100**, 7884 (1996). **Other strategies**: (Levine, 2016; Izmaylov, 2017).

Full- and Ab Initio Multiple Spawning



Credit: J. Michl and V. Bonacic-Koutecký, "Electronic Aspects of Organic Photochemistry". John Wiley and Sons, Inc., New York, 1990.

Gaussian-based quantum dynamics

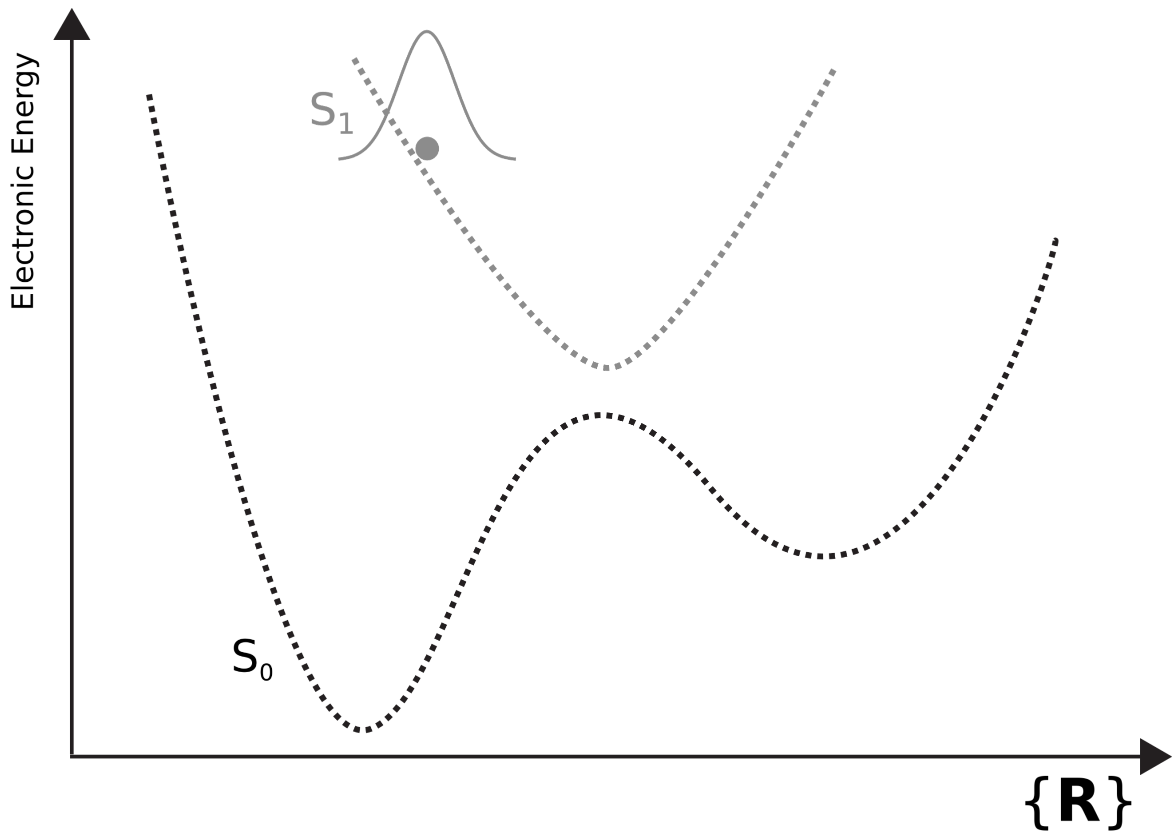


Full Multiple Spawning or ...
Formally exact method

Ab Initio Multiple Spawning (AIMS)
Approximate nuclear dynamics, but preserves important quantum effects.

For more information: M. Ben-Nun and T. J. Martínez, *Adv. Chem. Phys.*, **121**, 439 (2002). B. F. E. Curchod and T. J. Martínez, *Chem. Rev.*, **118**, 3305 (2018).

Gaussian-based quantum dynamics



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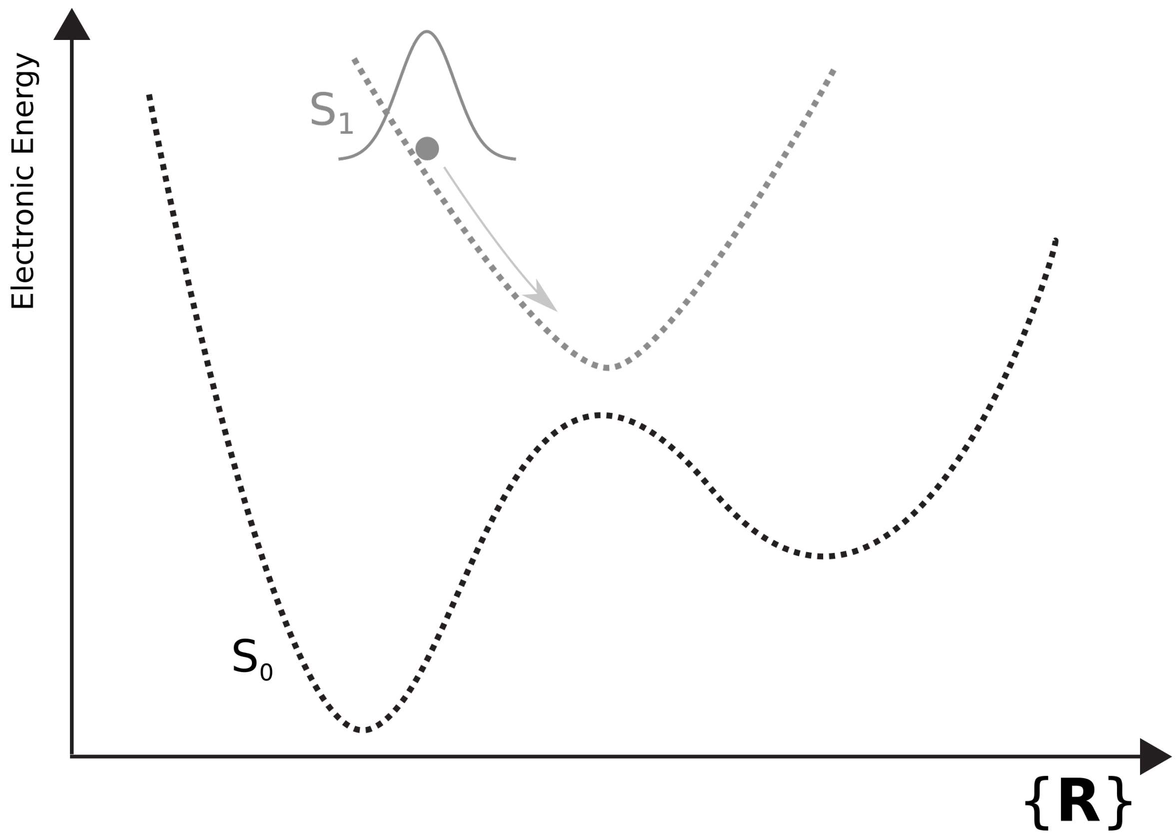

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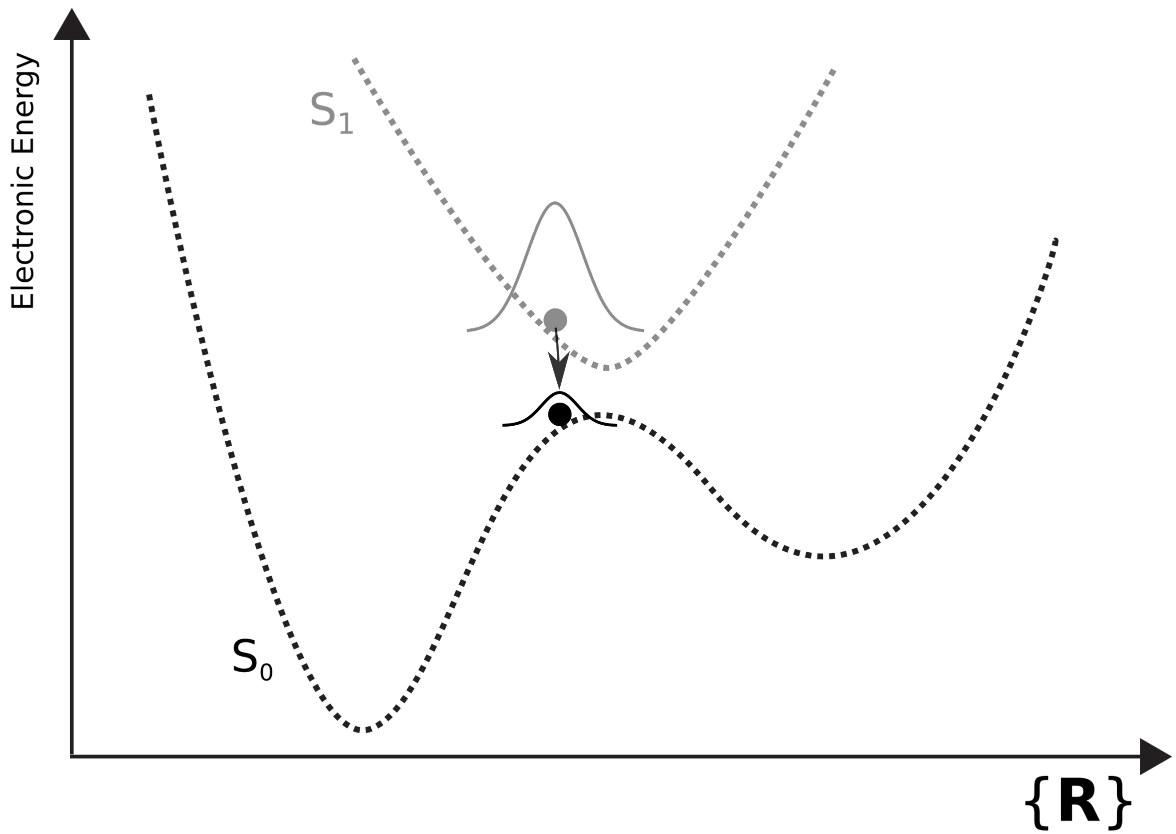

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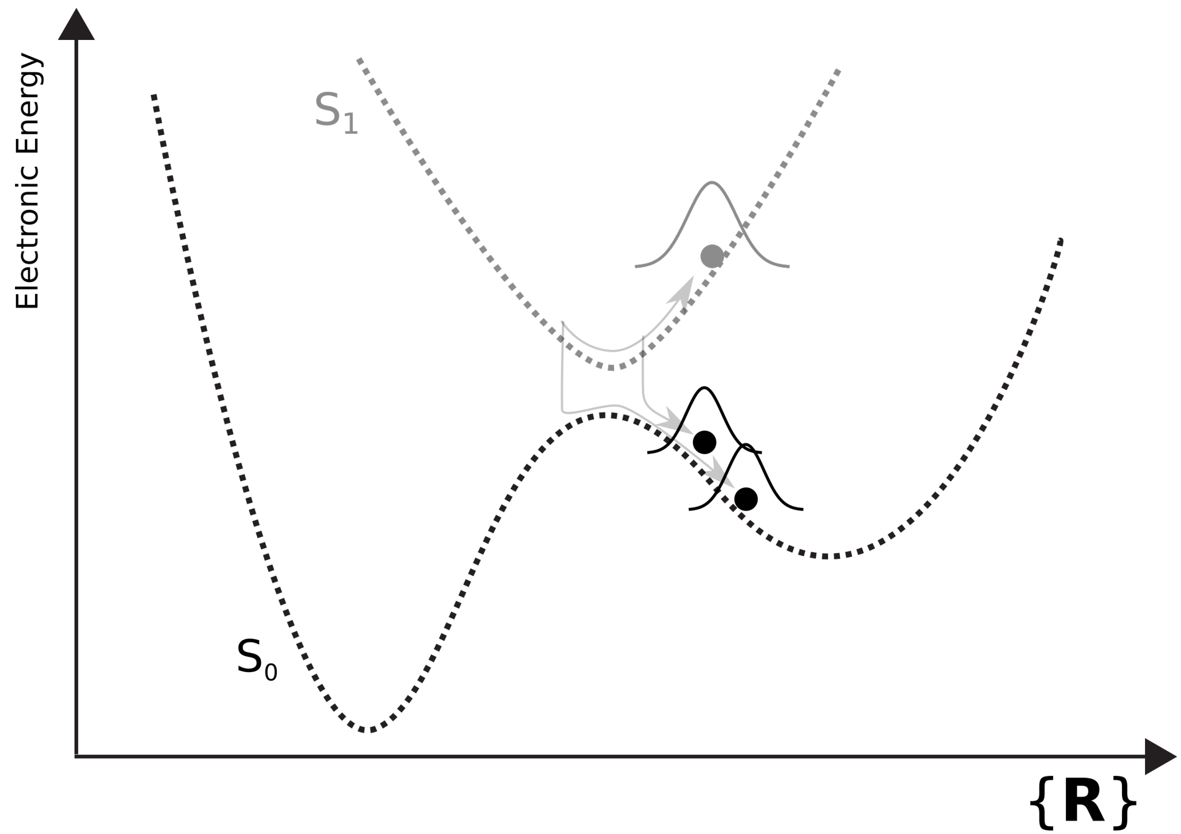

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Nonadiabatic molecular dynamics - FMS

Full Multiple Spawning in a nutshell

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},\mathbf{R},t) = \hat{H}_{mol}\Psi(\mathbf{r},\mathbf{R},t)$$

$\Downarrow$

Born-Huang: $\Psi(\mathbf{r},\mathbf{R},t) = \sum_J^{\infty} \Phi_J(\mathbf{r};\mathbf{R})\chi_J(\mathbf{R},t)$

$\Downarrow$

Eqs. of motion for the nuclei, $\dot{\chi}_I(\mathbf{R},t)$. (exact)

$\Downarrow$

FMS Ansatz: $\chi_I(\mathbf{R},t) = \sum_{j=1}^{N_I(t)} C_j^I(t)\chi_j^I\left(\mathbf{R};\overline{\mathbf{R}}_j^I(t),\overline{\mathbf{P}}_j^I(t),\overline{\gamma}_j^I(t),\boldsymbol{\alpha}\right)$

$\Downarrow$

Eqs. of motion for the complex amplitudes $C_j^I(t)$.
Gaussians center $\overline{\mathbf{R}}_j^I(t)$ and momentum $\overline{\mathbf{P}}_j^I(t)$ are evolved classically, while the phase $\overline{\gamma}_j^I(t)$ is evolved semiclassically.

Nonadiabatic molecular dynamics - FMS

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Nonadiabatic molecular dynamics - FMS

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Nonadiabatic molecular dynamics - FMS

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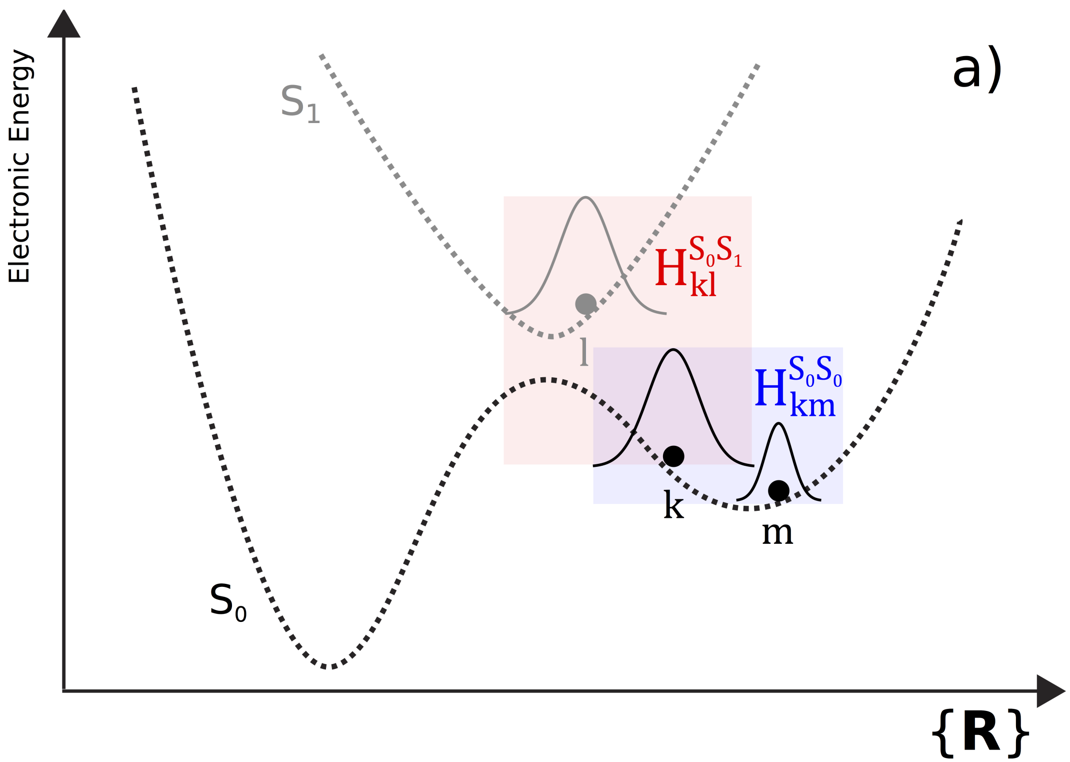
$$\Downarrow$$

$$\frac{d}{dt}\mathbf{C}^I(t) = -i(\mathbf{S}_{II}^{-1})\left[\left[\mathbf{H}_{II} - i\dot{\mathbf{S}}_{II}\right]\mathbf{C}^I + \sum_{J\neq I}\mathbf{H}_{IJ}\mathbf{C}^J\right]$$

Full/Ab Initio Multiple Spawning

Required electronic structure ingredients in FMS (exact)

$$H_{kk'}^{IJ} = \langle \chi_k^I | \hat{T}_{nuc} | \chi_{k'}^J \rangle_{\mathbf{R}} \delta_{IJ} + \langle \chi_k^I | E_I^{el} | \chi_{k'}^J \rangle_{\mathbf{R}} \delta_{IJ}$$
$$- \langle \chi_k^I | \sum_{\rho=1}^{3N} \frac{1}{M_\rho} \langle \Phi_I | \frac{\partial}{\partial R_\rho} | \Phi_J \rangle_{\mathbf{r}} \frac{\partial}{\partial R_\rho} | \chi_{k'}^J \rangle_{\mathbf{R}} - \langle \chi_k^I | \sum_{\rho=1}^{3N} \frac{1}{2M_\rho} \langle \Phi_I | \frac{\partial^2}{\partial R_\rho^2} | \Phi_J \rangle_{\mathbf{r}} | \chi_{k'}^I \rangle_{\mathbf{R}}$$



Electronic Properties

(adiabatic representation):

- $E_J^{el}(\mathbf{R})$
- $\mathbf{F}_J = -\nabla_{\mathbf{R}} E_J^{el}(\mathbf{R})|_{\mathbf{R}=\mathbf{R}(t)}$
- $\mathbf{d}_{JI}(\mathbf{R}) = \langle \Phi_J(\mathbf{R}) | \nabla_{\mathbf{R}} | \Phi_I(\mathbf{R}) \rangle_{\mathbf{r}}$
- $D_{JI}(\mathbf{R}) = \langle \Phi_J(\mathbf{R}) | \nabla_{\mathbf{R}}^2 | \Phi_I(\mathbf{R}) \rangle_{\mathbf{r}}$

Analytical model systems.

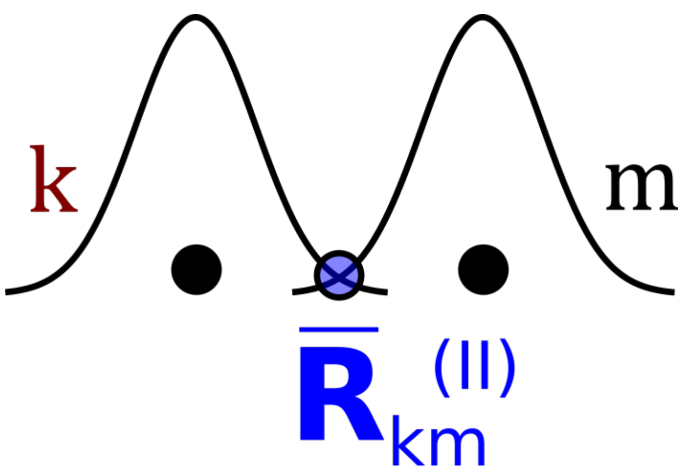
Adv. Chem. Phys., **121**, 439 (2002); *Chem. Rev.*, **118**, 3305 (2018).

Full/Ab Initio Multiple Spawning

Expansion of the electronic property around the centroid position $\overline{\mathbf{R}}_{km}^{(II)}$

$$E_I^{el}(\mathbf{R}) = E_I^{el}(\overline{\mathbf{R}}_{km}^{(II)}) + \sum_{\rho}^{3N}(R_\rho - \overline{R}_{\rho,km}^{(II)})\frac{\partial E_I^{el}(\mathbf{R})}{\partial R_\rho}\Big|_{R_\rho=\overline{R}_{\rho,km}^{(II)}}$$

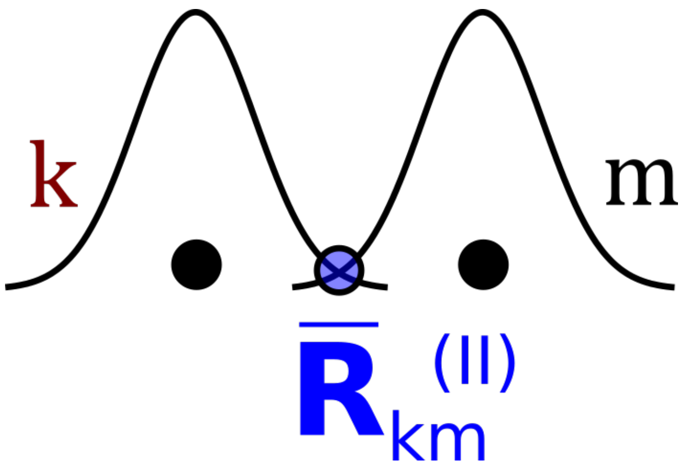
$$+\frac{1}{2}\sum_{\rho\rho'}^{3N}(R_\rho - \overline{R}_{\rho,km}^{(II)})\frac{\partial^2 E_I^{el}(\mathbf{R})}{\partial R_\rho \partial R_{\rho'}}\Big|_{R_\rho=\overline{R}_{\rho,km}^{(II)},R_{\rho'}=\overline{R}_{\rho',km}^{(II)}}(R_{\rho'} - \overline{R}_{\rho',km}^{(II)}) + \ldots$$



Full/Ab Initio Multiple Spawning

Approximation for the integrals:
saddle-point approximation of order 0!

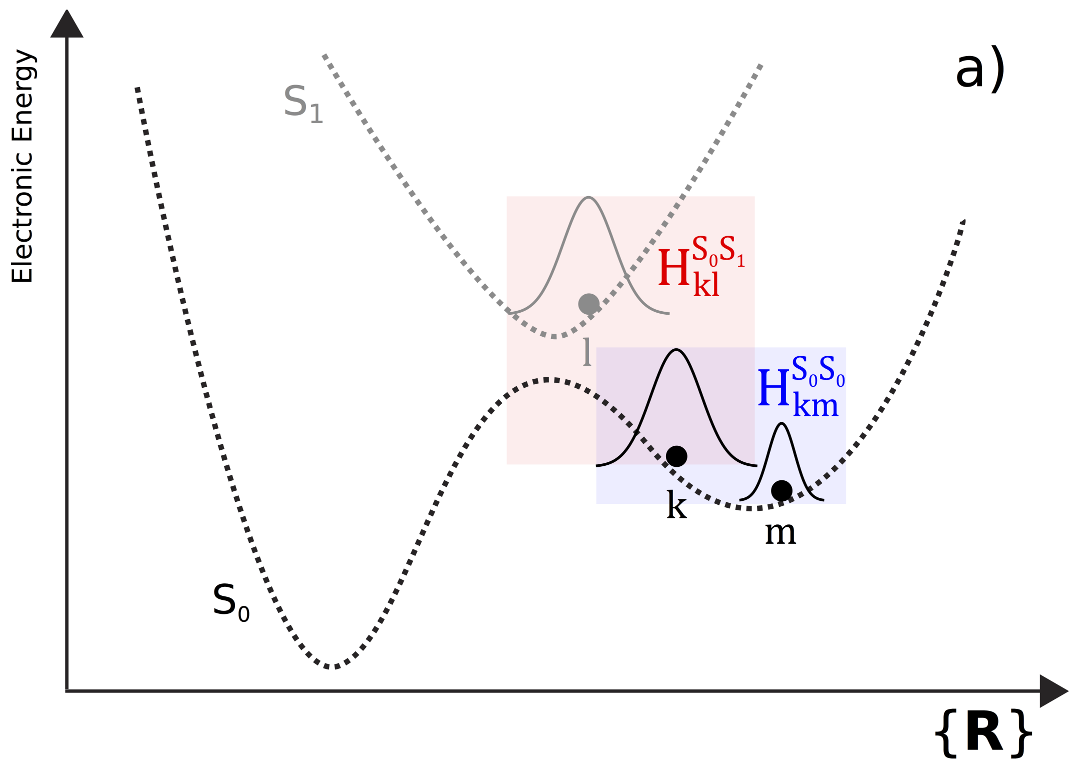
$$E_I^{el}(\mathbf{R}) \approx E_I^{el}(\overline{\mathbf{R}}_{km}^{(II)})$$



Full/Ab Initio Multiple Spawning

Required electronic structure ingredients in AIMS (approximated)

$$H^{IJ}_{kk'} = \langle \chi^I_k | \hat{T}_{nuc} | \chi^J_{k'} \rangle_{\mathbf{R}} \delta_{IJ} + E^{el}_I(\overline{\mathbf{R}}^{(IJ)}_{kk'}) \langle \chi^I_k | \chi^J_{k'} \rangle_{\mathbf{R}} \delta_{IJ} - \sum_{\rho=1}^{3N} \left(\mathbf{d}_{IJ}(\overline{\mathbf{R}}^{(IJ)}_{kk'}) \right)_\rho \langle \chi^I_k | \frac{1}{M_\rho} \frac{\partial}{\partial R_\rho} | \chi^J_{k'} \rangle_{\mathbf{R}}$$



Electronic Properties

(adiabatic representation):

$$\mathbf{R} = \mathbf{R}_{TBF} \text{ or } \overline{\mathbf{R}}^{(IJ)}$$

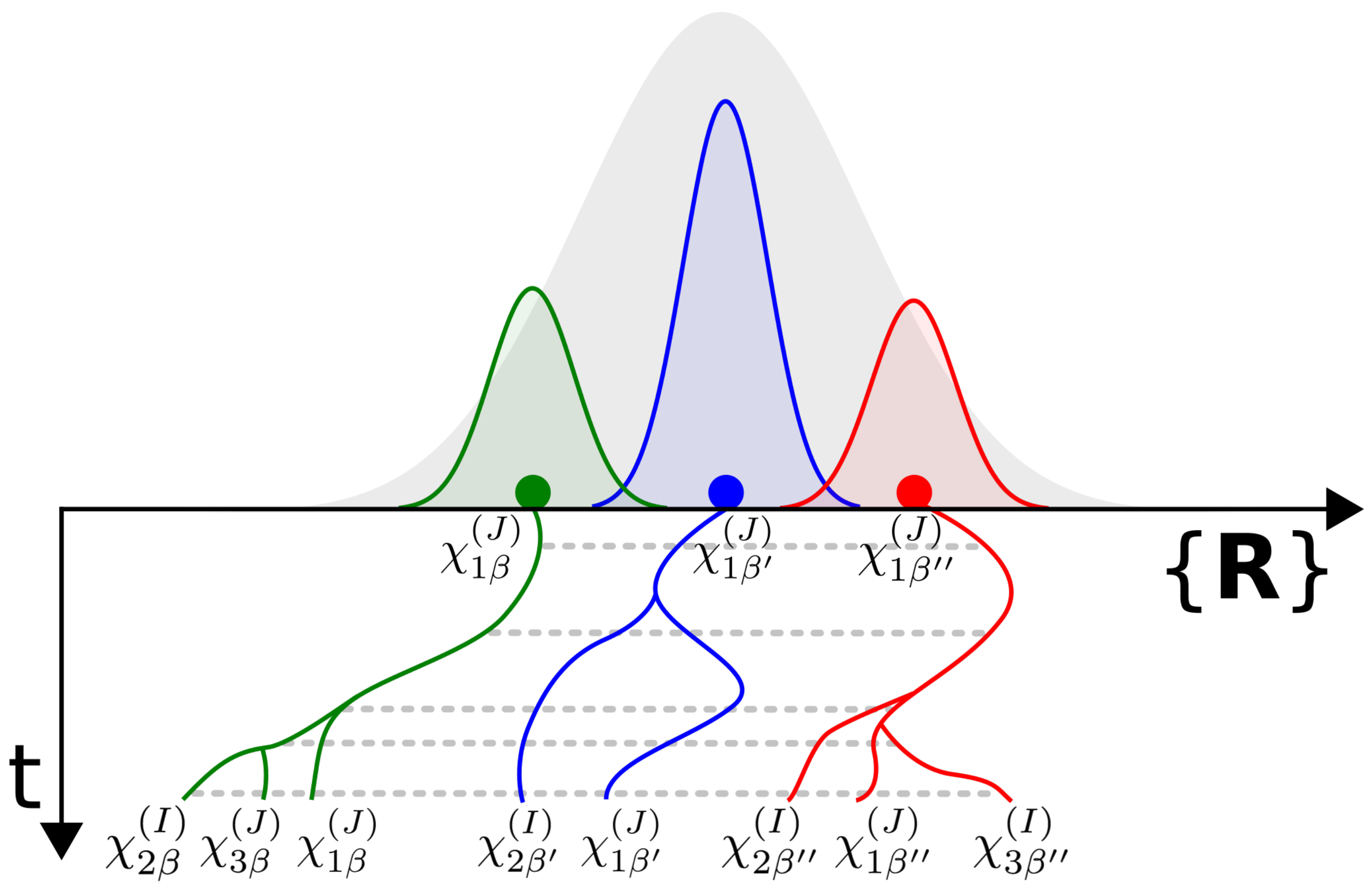
- $E^{el}_J(\mathbf{R})$
- $\mathbf{F}_J = -\nabla_{\mathbf{R}} E^{el}_J(\mathbf{R})|_{\mathbf{R}=\mathbf{R}_{TBF}(t)}$
- $\mathbf{d}_{JI}(\mathbf{R}) = \langle \Phi_J(\mathbf{R}) | \nabla_{\mathbf{R}} | \Phi_I(\mathbf{R}) \rangle_{\mathbf{r}}$

SA-CASSCF, MS-CASPT2, semiempirical methods.

Adv. Chem. Phys., **121**, 439 (2002); *Chem. Rev.*, **118**, 3305 (2018).

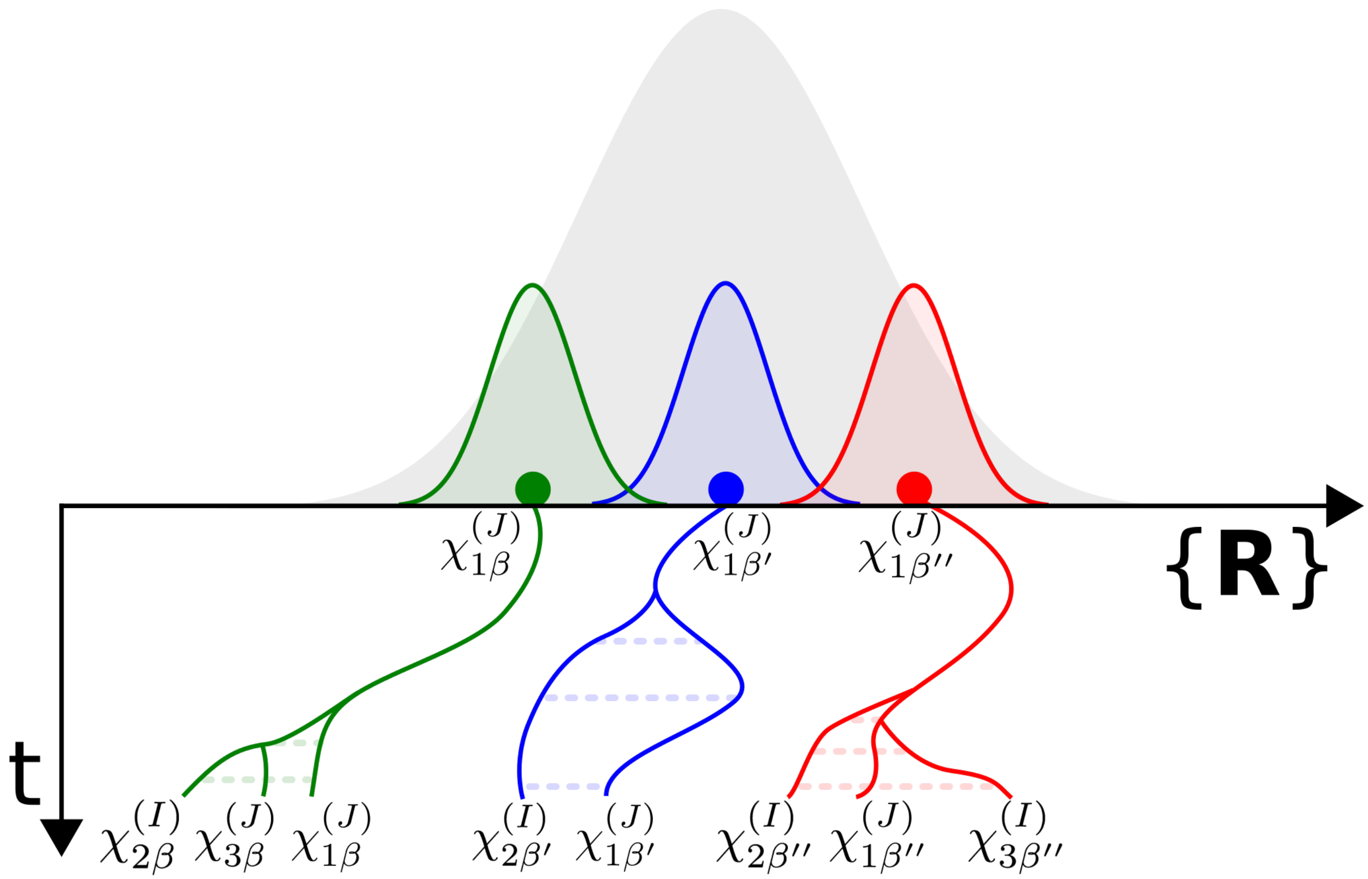
AIMS – Independent first generation approximation

FMS: all initial conditions are coupled from $t = 0$.

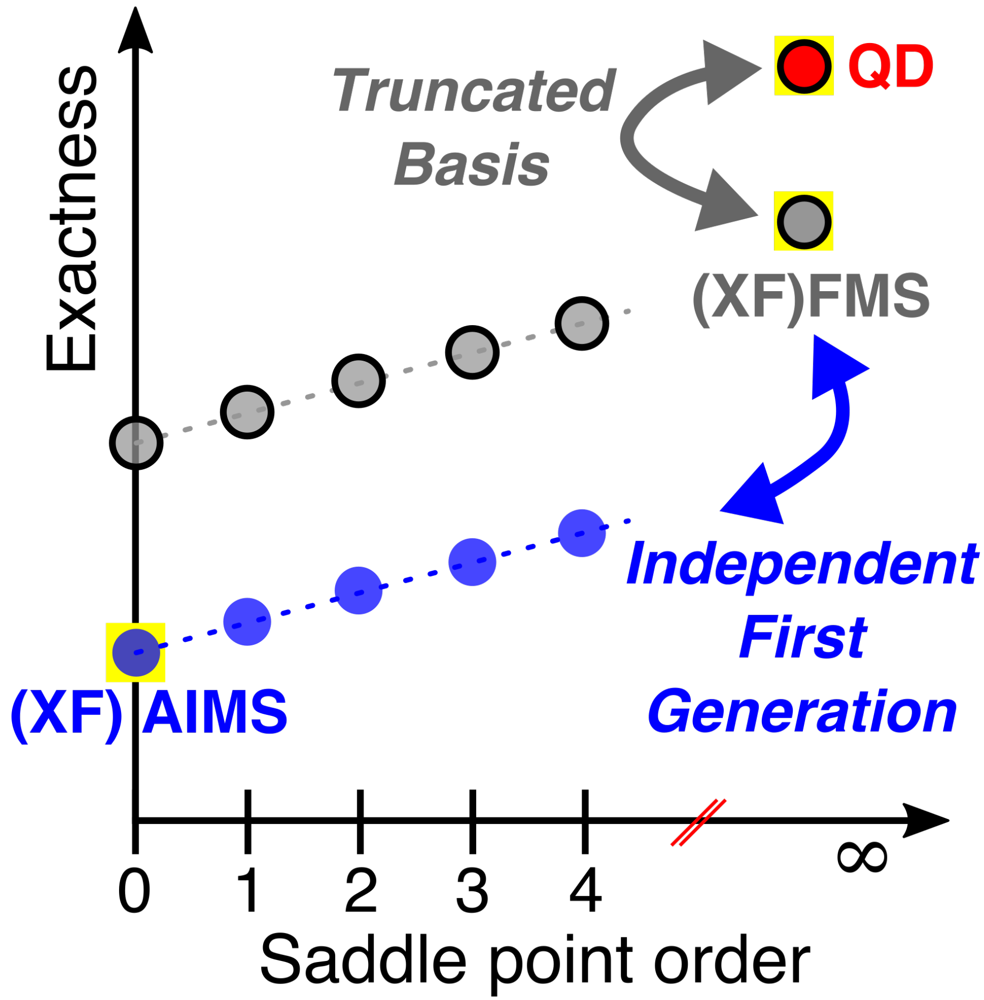


AIMS – Independent first generation approximation

AIMS: Independent First Generation Approximation (IFGA).

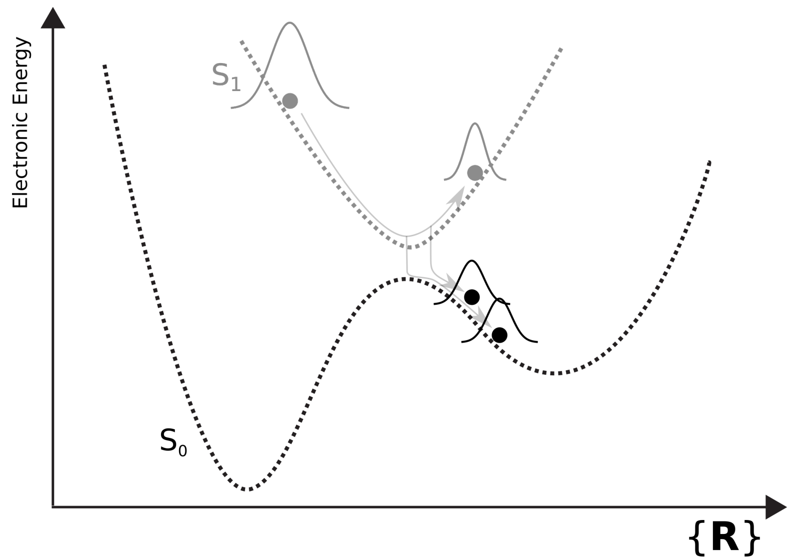


Summary: QD $\rightarrow$ FMS $\rightarrow$ AIMS



B. Mignolet and B. F. E. Curchod, *J. Chem. Phys.*, **148**, 134110 (2018).

Ab Initio Multiple Spawning – Summary



$$i\dot{\mathbf{C}}^I = -i(\mathbf{S}^{-1})_{II}\left[\left(\mathbf{H}_{II} - i\dot{\mathbf{S}}_{II}\right)\mathbf{C}^I + \sum_{J\neq I}\mathbf{H}_{IJ}\mathbf{C}^J\right]$$

using the **saddle-point approximation**

$$H^{IJ}_{kk'} = \langle\chi^{(I)}_k|\hat{T}_{nuc}|\chi^{(J)}_{k'}\rangle_{\mathbf{R}}\delta_{IJ} + E^{el}_I(\overline{\mathbf{R}}^{(IJ)}_{kk'})\langle\chi^{(I)}_k|\chi^{(J)}_{k'}\rangle_{\mathbf{R}}\delta_{IJ} - \sum_{\rho=1}^{3N}\left(\mathbf{d}_{IJ}(\overline{\mathbf{R}}^{(IJ)}_{kk'})\right)_\rho\langle\chi^{(I)}_k|\frac{1}{M_\rho}\frac{\partial}{\partial R_\rho}|\chi^{(J)}_{k'}\rangle_{\mathbf{R}}$$

and the **independent first generation**.