

Density Functional Theory: from theory to Applications

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December 7, 2010

Pseudopotentials

Hamann-Schlüter-Chiang pseudopotentials

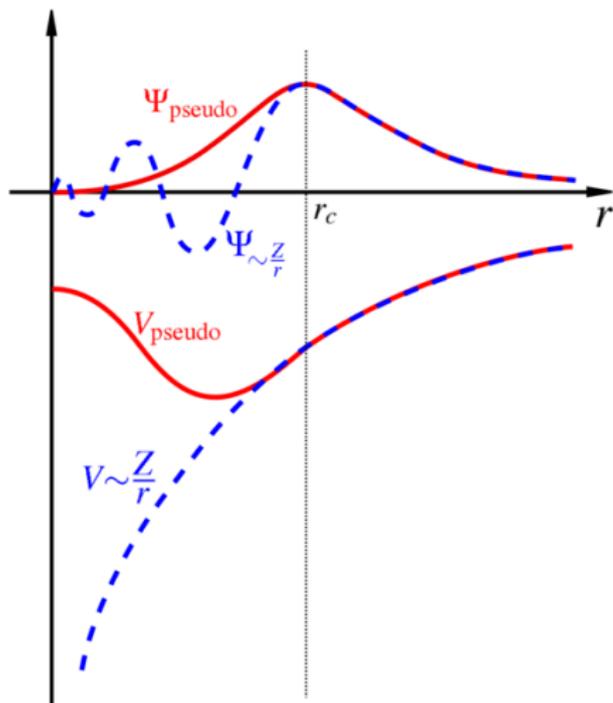
Bachelet, Kerker, Martin-Troulliers

Unifying molecular dynamics and electronic structure

Route 1

Route 2

- ▶ Only the chemically active electrons are considered explicitly.
- ▶ The core electrons are eliminated within the frozen-core approximation and are considered together with the nuclei as rigid non-polarizable ion cores.
- ▶ The Pauli repulsion largely cancels the attractive parts of the true potential in the core region, and is built into the therefore rather weak pseudopotentials.

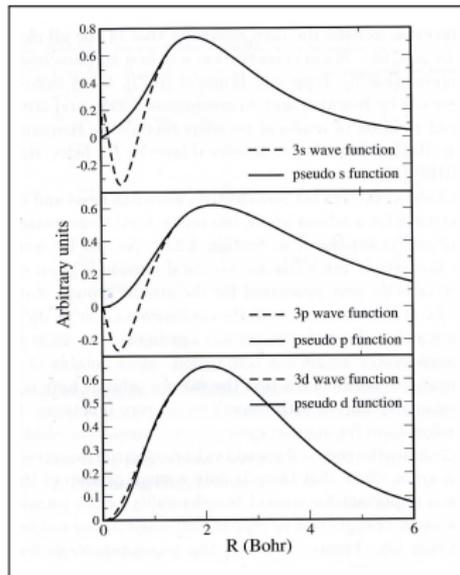


Why Pseudopotentials?

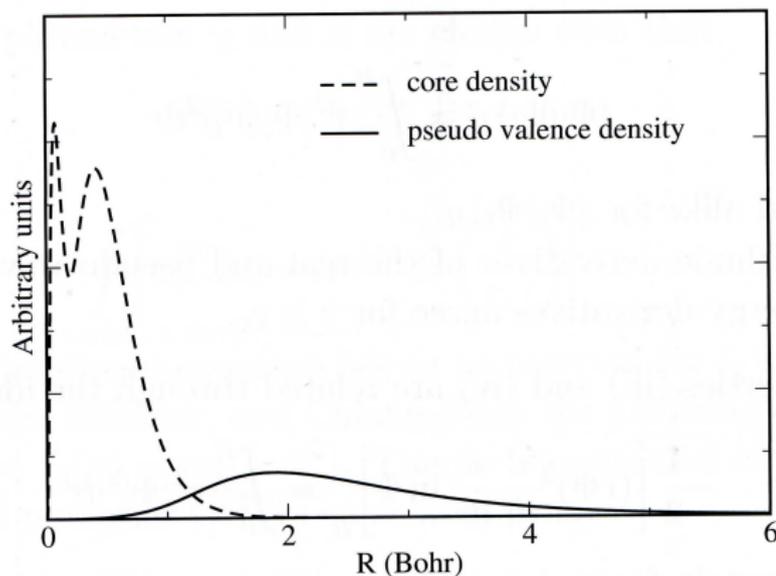
- ▶ Reduction of the number of electron in the systems, faster calculation for large systems
- ▶ Relativistic effects depending on the core electrons treated incorporated indirectly in the pseudopotentials
- ▶ In the frame of plane wave basis set: reduction of the basis set size introducing smoother functions which requires a lower cutoff
- ▶ The number of plane waves needed for a certain accuracy increases with the square of the nuclear charge.

Norm-conserving pseudopotentials

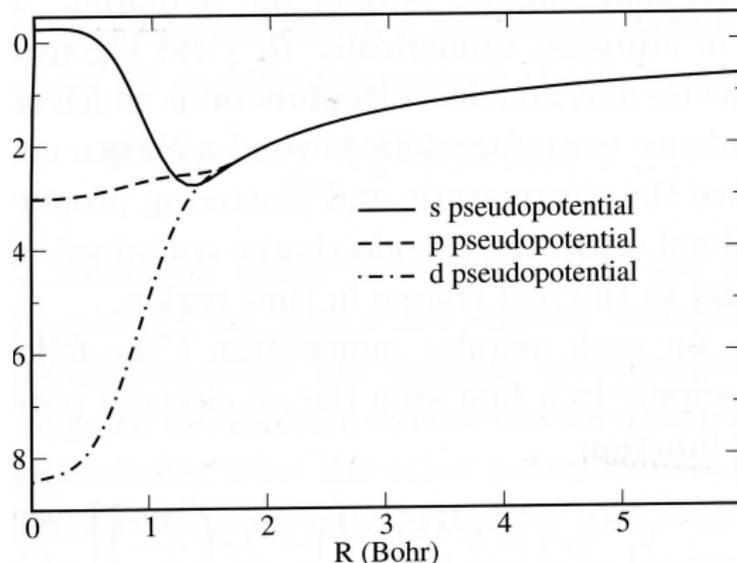
Norm-conserving pseudopotentials conserves the normalization of the pseudo wf in the core region so that the wf outside resembles that of the all-electrons as closely as possible.



Valence and pseudo wf of a Si atom, generated according to Martin-Troullier scheme.



Ground state core density (dashed line) and pseudo valence density (solid line) for a Si atom.



Note: The pseudopotentials converge to the limit $-Z/r$ outside the core radius.

Hamann-Schlüter-Chiang conditions¹

Norm-conserving pseudos are derived from atomic reference state:

$$(T + V^{AE})|\Psi_I\rangle = \epsilon_I|\Psi_I\rangle. \quad (1)$$

This is replaced by the "valence electrons only"

$$(T + V^{val})|\Phi_I\rangle = \tilde{\epsilon}_I|\Phi_I\rangle. \quad (2)$$

Imposing the following:

- ▶ $\epsilon_I = \tilde{\epsilon}_I$ for a chosen prototype atomic configuration.
- ▶ $\Psi_I(r) = \Phi_I(r)$ for $r \geq r_c$.
- ▶ Norm conservation, $\langle \Phi_I | \Phi_I \rangle_R = \langle \Psi_I | \Psi_I \rangle_R$ for $R \geq r_c$.
- ▶ Log derivative of Φ_I equal to that of Ψ_I .

¹Hamann-Schlüter-Chiang, *Phys. Rev. Lett.*, 43, 1494 (1979) 

Hamann-Schlüter-Chiang recipe

- ▶ First step: the all-electron wf is multiplied by a smoothing function f_1 to remove strongly attractive and singular part of the potential:

$$V_l^{(1)}(r) = V^{AE}(r) \left[1 - f_1 \left(\frac{r}{r_{c,l}} \right) \right] \quad (3)$$

- ▶ Then a function f_2 is added in order to obtain $\epsilon_l = \tilde{\epsilon}_l$

$$V_l^{(2)}(r) = V_l^{(1)}(r) + c_l f_2 \left(\frac{r}{r_{c,l}} \right) \quad (4)$$

$$\left(T + V_l^{(2)}(r) \right) w_l^{(2)}(r) = \tilde{\epsilon}_l w_l^{(2)}(r) \quad (5)$$

- ▶ The valence wf is defined as

$$\Phi_l(r) = -\gamma_l \left[w_l^{(2)}(r) + \delta_l r^{l+1} f_3 \left(\frac{r}{r_{c,l}} \right) \right] \quad (6)$$

where γ_l and δ_l are chosen such that $\Phi_l(r) \rightarrow \Psi_l(r)$ for $R \geq r_c$.

Hamann-Schlüter-Chiang recipe

- ▶ Given Φ_l and $\tilde{\epsilon}_l$ the equation:

$$(T + V^{val})|\Phi_l\rangle = \tilde{\epsilon}_l|\Phi_l\rangle.$$

is inverted to get $V^{val}(r)$.

Hamann-Schlüter-Chiang chose $f_1(x) = f_2(x) = f_3(x) = \exp[-x^4]$.

$$V_l^{PP}(r) = V_l^{val}(r) - V_H(n_V) - V_{xc}(n_V) \quad (7)$$

The total atomic pseudopotential then takes the form of a sum over all angular momentum channels:

$$V^{PP}(\mathbf{r}) = \sum_L V_L^{PP}(r) \mathbf{P}_L(\omega) \quad (8)$$

where $\mathbf{P}_L(\omega)$ is the projector on the angular momentum state L , defined by $\{l, m\}$ and ω are angular variables.

Bachelet-Hamann-Schlüter pseudopotentials

Bachelet et proposed an analytic form to fit the pseudos generated by Hamann-Schlüter-Chiang of the form:

$$V^{PP}(r) = V^{core}(r) + \sum_L \Delta V_L^{ion}(r) \quad (9)$$

$$V^{core}(r) = -\frac{Z_V}{r} \left[\sum_{i=1}^2 c_i^{core} \operatorname{erf}(\sqrt{\alpha_i^{core}} r) \right] \quad (10)$$

$$V_L^{ion}(r) = \sum_{i=1}^3 (A_i + r^2 A_{i+3}) \exp[-\alpha_i r^2] \quad (11)$$

the advantage here is that this form allow an easy implementation in plane-wave code, since the Fourier transform can be also written analytically.

Kerker pseudopotentials

In the Kerker approach² pseudopotentials are constructed to satisfy HSC conditions, but replacing the AE wf inside r_c with a smooth analytic function that matches the AE wf at r_c .

- ▶ r_c is generally larger than that used in HSC

The analytic form proposed by Kerker is

$$\Phi_l(r) = r^{l+1} \exp[p(r)] \text{ for } r < r_{c,l} \quad (12)$$

with l -dependent cut-off radii $r_{c,l}$ and

$$p(r) = \alpha r^4 + \beta r^3 + \gamma r^2 + \delta \quad (13)$$

The method of Kerker was generalized by Troullier and Martins to polynomials of higher order³

²Kerker, *J. of Phys. C* 13; L189 (1980)

³*Phys. rev. B*, 43: 1993. (1991).

An Example: pseudos for carbon

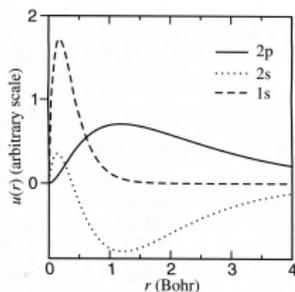


Fig. 4.6. All-electron wave functions $u(r) = r\Psi(r)$ for the carbon atom in the ground state.

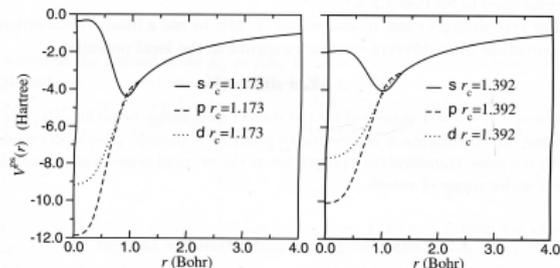
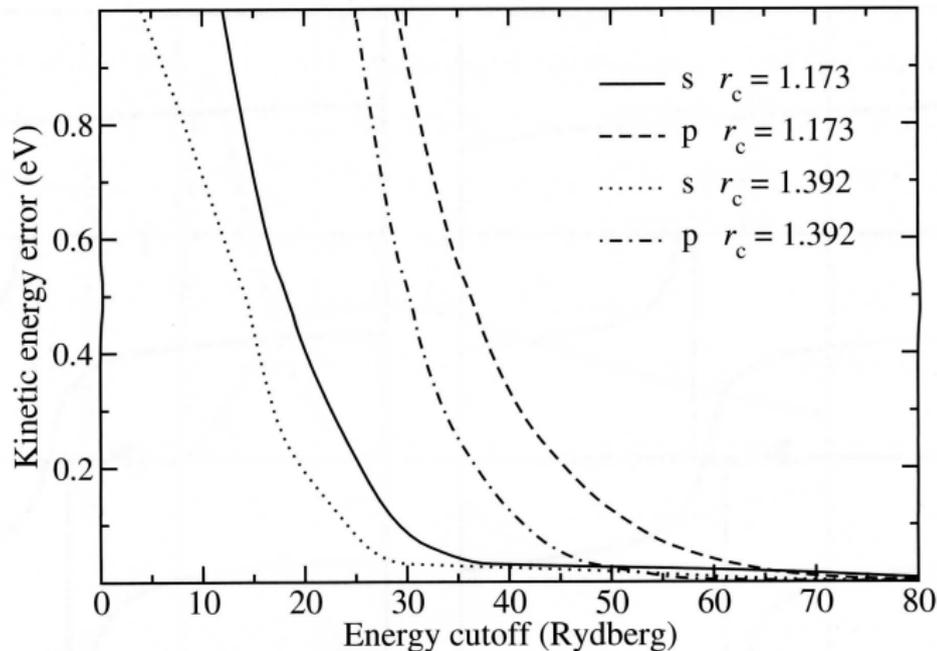


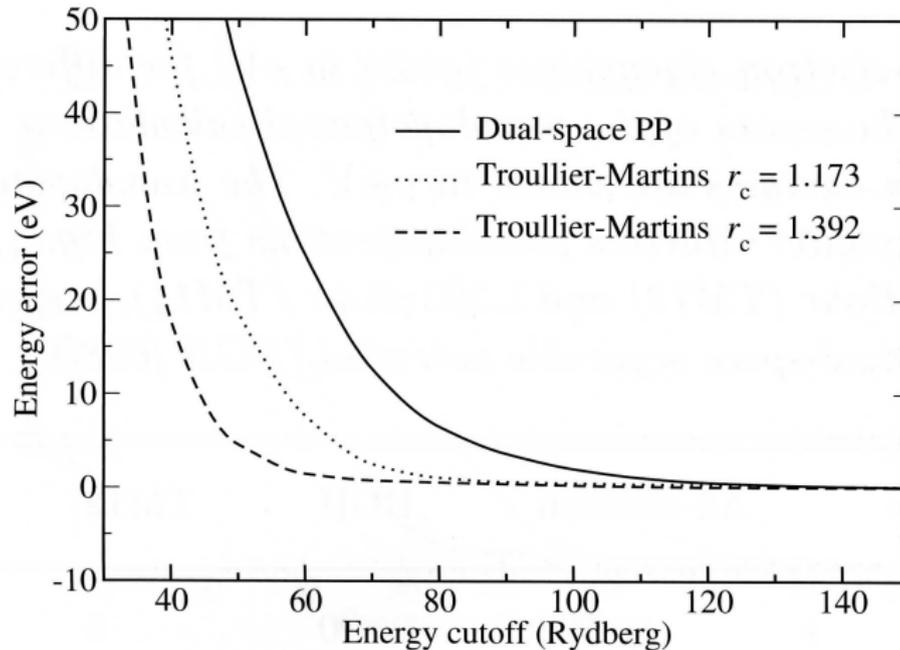
Fig. 4.7. Two sets of Troullier-Martins pseudopotentials for carbon generated by using two different cutoff radii r_c as indicated in the panels.

Martin-Troulliers
pseudopotential for carbon in
the LDA.

reference configuration:
 $1s^2 2s^2 2p^2$



Convergence of the kinetic energy for carbon atom as function of the cutoff.



Convergence of the total energy of diamond as function of the cutoff.

Unifying molecular dynamics and electronic structure

Unifying molecular dynamics and electronic structure

Starting point: the non-relativistic Schrödinger equation for electron and nuclei.

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}; t) = H\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}; t) \quad (14)$$

where H is the standard Hamiltonian:

$$H = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \quad (15)$$

$$+ \frac{1}{4\pi\epsilon_0} \sum_{i<j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I,i} \frac{e^2 Z_I}{|\mathbf{R}_I - \mathbf{r}_i|} + \frac{1}{4\pi\epsilon_0} \sum_{I<J} \frac{e^2 Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (16)$$

$$= -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{n-e}(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \quad (17)$$

$$= -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \quad (18)$$

► **Route 1:**

- 1) The electronic problem is solved in the *time-independent* Schrodinger eq.
- 2) from here the **adiabatic approximation** for the nuclei is derived, and as a special case the **Born-Oppenheimer dynamics**.
- 3) The classical limit leads then to the **classical molecular dynamics** for the nuclei.

Goal: derive the classical molecular dynamics. As intermediate two variant of *ab initio* molecular dynamics are derived.

- Solve the electronic part for fixed nuclei

$$H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\Psi_k = E_k(\{\mathbf{R}_i\})\Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \quad (19)$$

where $\Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})$ are a set of orthonormal solutions, satisfying:

$$\int \Psi_k^*(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\Psi_l(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})d\mathbf{r} = \delta_{kl} \quad (20)$$

Knowing the *adiabatic solutions* to the electronic problem, the total wavefunction can be expanded as:

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}, t) = \sum_{l=0}^{\infty} \Psi_l(\{\mathbf{r}_i\}, \{\mathbf{R}_i\})\chi_l(\{\mathbf{R}_i\}, t) \quad (21)$$

Eq.21 is the *ansatz* introduced by Born in 1951.

Inserting (21) into Eq.(14) we obtain:

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_i\}) \right] \chi_k + \sum_I C_{kI} \chi_I = i\hbar \frac{\partial}{\partial t} \chi_k \quad (22)$$

where:

$$C_{kl} = \int \Psi_k^* \left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \right] \Psi_l d\mathbf{r} + \quad (23)$$

$$+ \frac{1}{M_I} \sum_I \left\{ \int \Psi_k^* [-i\hbar \nabla_I] \Psi_l d\mathbf{r} \right\} [-i\hbar \nabla_I] \quad (24)$$

is the exact non-adiabatic coupling operator.

- ▶ The adiabatic approximation to the full problem Eq.22 is obtained considering only the diagonal terms:

$$C_{kk} = -\sum_I \frac{\hbar^2}{2M_I} \int \Psi_k^* \nabla_I^2 \Psi_k d\mathbf{r} \quad (25)$$

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_i\}) + C_{kk}(\{\mathbf{R}_i\}) \right] \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k \quad (26)$$

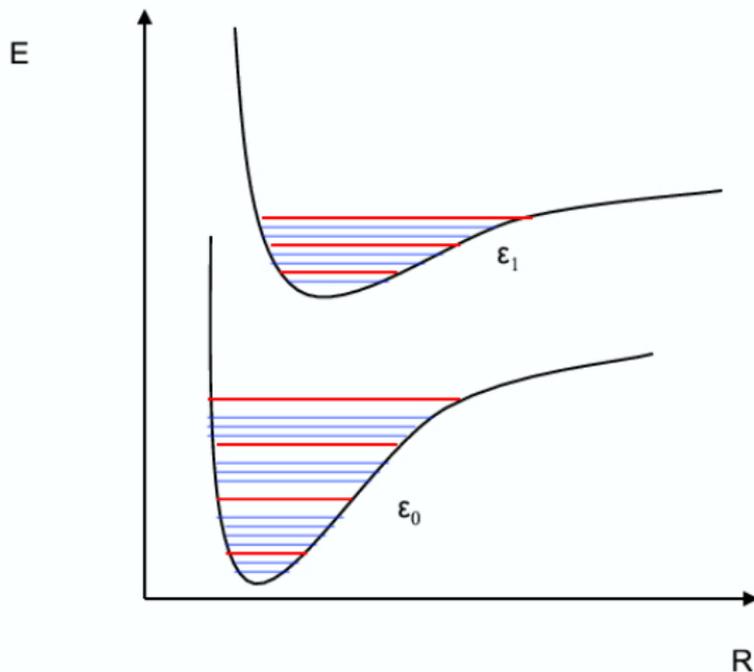
The motion of the nuclei proceed without changing the quantum state, k , of the electronic subsystem during the evolution. The coupled wavefunction can be simplified as:

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}, t) \approx \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_i\}) \chi_k(\{\mathbf{R}_i\}, t) \quad (27)$$

the ultimate simplification consist in neglecting also the correction term $C_{kk}(\{\mathbf{R}_i\})$, so that

$$\left[-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 + E_k(\{\mathbf{R}_i\}) \right] \chi_k = i\hbar \frac{\partial}{\partial t} \chi_k \quad (28)$$

This is the **Born-Oppenheimer approximation**.



On each Born-Oppenheimer surface, the nuclear eigenvalue problem can be solved, which yields a set of levels (rotational and vibrational in the nuclear motion) as illustrated in the figure.

The next step is to derive the classical molecular dynamics for the nuclei. The route we take is the following:

$$\chi_k(\{\mathbf{R}_i\}, t) = A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar] \quad (29)$$

the amplitude A_k and the phase S_k are both real and $A_k > 0$. Next we substitute the expression for χ_k into eq. 28.

$$\left[-\sum_i \frac{\hbar^2}{2M_i} \nabla_i^2 + E_k(\{\mathbf{R}_i\}) \right] A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar] = \quad (30)$$

$$i\hbar \frac{\partial}{\partial t} (A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar]) \quad (31)$$

$$-\sum_i \frac{\hbar^2}{2M_i} \nabla_i (\nabla_i (A_k \exp[iS_k/\hbar])) + E_k A_k \exp[iS_k/\hbar] = \quad (32)$$

$$i\hbar \frac{\partial A_k}{\partial t} \exp[iS_k/\hbar] + i\hbar \frac{i}{\hbar} \frac{\partial S_k}{\partial t} A_k \exp[iS_k/\hbar] \quad (33)$$

$$-\sum_i \frac{\hbar^2}{2M_i} \nabla_i \left(\nabla_i A_k \exp[iS_k/\hbar] + A_k \frac{i}{\hbar} \nabla S_k \exp[iS_k/\hbar] \right) + E_k A_k \exp[iS_k/\hbar] = \quad (34)$$

$$i\hbar \frac{\partial A_k}{\partial t} \exp[iS_k/\hbar] - \frac{\partial S_k}{\partial t} A_k \exp[iS_k/\hbar] \quad (35)$$

$$-\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 A_k - \sum_I \frac{\hbar^2}{2M_I} \nabla_I A_k \frac{i}{\hbar} \nabla_I S_k - \sum_I \frac{\hbar^2}{2M_I} \nabla_I A_k \frac{i}{\hbar} \nabla_I S_k \quad (36)$$

$$-\sum_I \frac{\hbar^2}{2M_I} A_k \left(\frac{i}{\hbar}\right)^2 (\nabla S_k)^2 - \sum_I \frac{\hbar^2}{2M_I} A_k \frac{i}{\hbar} \nabla^2 S_k + E_k A_k = \quad (37)$$

$$i\hbar \frac{\partial A_k}{\partial t} - \frac{\partial S_k}{\partial t} A_k \quad (38)$$

Separating the real and the imaginary parts, we obtain:

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + E_k = - \sum_I \frac{\hbar^2}{2M_I} \frac{\nabla_I^2 A_k}{A_k} \quad (39)$$

$$\frac{\partial A_k}{\partial t} + \sum_I \frac{1}{M_I} \nabla_I A_k \nabla_I S_k + \sum_I \frac{1}{2M_I} A_k \nabla^2 S_k = 0 \quad (40)$$

If we consider the equation for the phase:

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + E_k = - \sum_I \frac{\hbar^2}{2M_I} \frac{\nabla_I^2 A_k}{A_k} \quad (41)$$

it is possible to take the classical limit $\hbar \rightarrow 0$ which gives the equation:

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + E_k = 0 \quad (42)$$

which is isomorphic to Hamilton-Jacobi of classical mechanics:

$$\frac{\partial S_k}{\partial t} + H_k(\{\mathbf{R}_I\}, \{\nabla_I S_k\}) = 0 \quad (43)$$

with the classical Hamiltonian function

$$H_k(\{\mathbf{R}_I\}, \{\mathbf{P}_I\}) = T(\{\mathbf{P}_I\}) + V_k(\{\mathbf{R}_I\}) \quad (44)$$

With the connecting transformation: $\mathbf{P}_I = \nabla_I S_k$.

► **Route 2:**

- 1) Maintain the **quantum-mechanical time evolution for the electrons** introducing the separation for the electronic and nuclear wf function in a time-dependent way
- 2) **Time-dependent self consistent field (TDSCF)** approach is obtained.
- 3) **Ehrenfest dynamics** (and as special case Born-Oppenheimer dynamics)
- 4) The classical limit leads then to the **classical molecular dynamics** for the nuclei.

It is possible to follow an alternative route in order to maintain the dynamics of the electron.

$$\Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) \approx \Psi(\{\mathbf{r}_i\}, t) \chi(\{\mathbf{R}_I\}, t) \exp\left[\frac{i}{\hbar} \int_{t_0}^t \tilde{E}_e(t') dt'\right] \quad (45)$$

where:

$$\tilde{E}_e = \int \Psi^*(\{\mathbf{r}_i\}, t) \chi^*(\{\mathbf{R}_I\}, t) H_e \Psi(\{\mathbf{r}_i\}, t) \chi(\{\mathbf{R}_I\}, t) d\mathbf{r} d\mathbf{R} \quad (46)$$

Inserting this separation ansatz into

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t) = H \Phi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}; t)$$

and multiplying from the left by Ψ^* and by χ^* we obtain

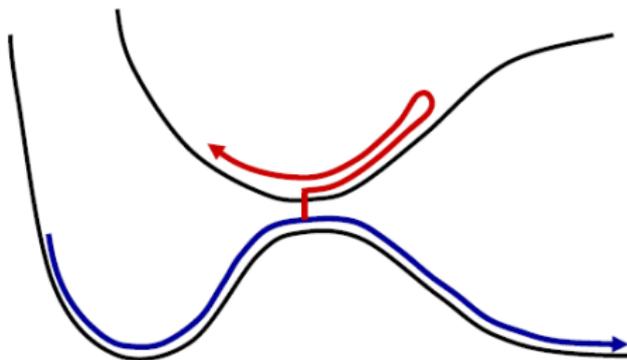
$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi \quad (47)$$

$$+ \left\{ \int \chi^* (\{\mathbf{R}_I\}, t) V_n e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi (\{\mathbf{R}_I\}, t) d\mathbf{R} \right\} \Psi \quad (48)$$

$$\hbar \frac{\partial \chi}{\partial t} = - \sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \chi \quad (49)$$

$$+ \left\{ \int \Psi^* (\{\mathbf{r}_i\}, t) H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi (\{\mathbf{r}_i\}, t) d\mathbf{r} \right\} \chi \quad (50)$$

This set of time-dependent Schrodinger equations define the basis of **time-dependent self-consistent field (TDSCF)** method. Both electrons and nuclei moves quantum-mechanically in time-dependent effective potentials.



- Classical motion induces electronic transitions
 - Quantum state determines classical forces
- Quantum – Classical Feedback: Self-Consistency

Using the same trick as before of writing

$$\chi_k(\{\mathbf{R}_i\}, t) = A_k(\{\mathbf{R}_i\}, t) \exp[iS_k(\{\mathbf{R}_i\}, t)/\hbar] \quad (51)$$

we obtain

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + \int \Psi^* H_e \Psi d\mathbf{r} = - \sum_I \frac{\hbar^2}{2M_I} \frac{\nabla_I^2 A_k}{A_k} \quad (52)$$

$$\frac{\partial A_k}{\partial t} + \sum_I \frac{1}{M_I} \nabla_I A_k \nabla_I S_k + \sum_I \frac{1}{2M_I} A_k \nabla^2 S_k = 0 \quad (53)$$

And in the classical limit $\hbar \rightarrow \infty$

$$\frac{\partial S_k}{\partial t} + \sum_I \frac{1}{2M_I} (\nabla S_k)^2 + \int \Psi^* H_e \Psi d\mathbf{r} = 0. \quad (54)$$

- ▶ The nuclei move according to *classical* mechanics in an effective potential (Ehrenfest potential) given by the quantum dynamics of the electrons obtained by solving the time-dependent Schrodinger equation for the electrons.

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + \left\{ \int \chi^* (\{\mathbf{R}_I\}, t) V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) d\mathbf{R} \right\} \Psi \quad (55)$$

Note: the equation (54) still contains the full quantum-mechanics nuclear wavefunction $\chi(\{\mathbf{R}_I\}, t)$. The classical reduction is obtained by:

$$\int \chi^* (\{\mathbf{R}_I\}, t) \mathbf{R}_I \chi(\{\mathbf{R}_I\}, t) d\mathbf{R} \rightarrow \mathbf{R}_I(t) \quad (56)$$

for $\hbar \rightarrow 0$.

The classical limits leads to a time-dependent wave equation for the electrons

$$i\hbar \frac{\partial \Psi}{\partial t} = - \sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \Psi + V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \Psi \quad (57)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \quad (58)$$

- ▶ Feedback between the classical and quantum degrees of freedom is incorporated in both direction, even though in a mean field sense.
- ▶ These equations are called Ehrenfest dynamics in honor to Paul Ehrenfest who was the first to address the problem of how Newtonian classical dynamics of point particles can be derived from Schrodinger time-dependent wave equation.

Difference between Ehrenfest dynamics and Born-Oppenheimer molecular dynamics:

- ▶ In ED the electronic subsystem evolves explicitly in time, according to a time-dependent Schrodinger equation
- ▶ In ED transition between electronic states are possible. This can be showed expressing the electronic wavefunction in a basis of electronic states

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) \quad (59)$$

where

$$\sum_{I=0}^{\infty} |c_I(t)|^2 = 1 \quad (60)$$

and one possible choice for the basis functions $\{\Psi_k\}$ is obtained solving the time-independent Schrodinger equation:

$$H_e(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) = E_k(\{\mathbf{R}_I\}) \Psi_k(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}). \quad (61)$$

The Ehrenfest dynamics reduces to the Born-Oppenheimer molecular dynamics if only one term is considered in the sum:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$$

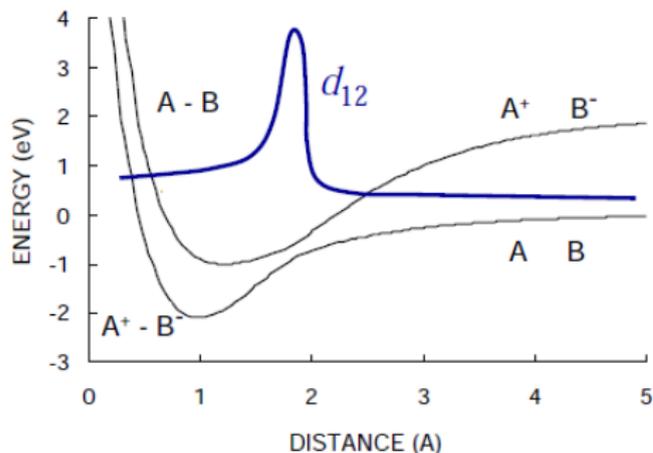
namely:

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \Psi_0 \text{ground state adiabatic wavefunction} \quad (62)$$

This should be a good approximation if the energy difference between Ψ_0 and the first excited state Ψ_1 is large everywhere compared to the thermal energy scale $K_B T$.

In this approximation the nuclei move on a single adiabatic potential energy surface, $E_0(\{\mathbf{R}_I\})$.

Ionic Molecule (alkali halide)



Nonadiabatic Coupling:
$$d_{12} = \langle \varphi_1 | \partial \varphi_2 / \partial X \rangle$$

Classical trajectory calculations on global potential energy surfaces

In BO one can think to fully decouple the task of generating classical nuclear dynamics from the task of computing the quantum potential energy surface.

- ▶ E_0 is computed for many different $\{\mathbf{R}_I\}$
- ▶ data points fitted to analytical function
- ▶ Newton equation of motion solved on the computed surfaces for different initial conditions

Problem: **dimensionality bottleneck**. It has been used for scattering and chemical reactions of small systems in vacuum, but is not doable when nuclear degrees of freedom increase.

Force Field - based molecular dynamics

One possible solution to the dimensionality bottleneck is the force field based MD.

$$V_e^E \approx V_e^{FF} = \sum_{I=1}^N v_1(\mathbf{R}_I) + \sum_{I<J}^N v_2(\mathbf{R}_I, \mathbf{R}_J) + \quad (63)$$

$$\sum_{I<J<K}^N v_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \dots \quad (64)$$

The equation of motion for the nuclei are:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{FF}(\{\mathbf{R}_I(t)\}). \quad (65)$$

The electrons follow adiabatically the classical nuclear motion and can be integrated out. The nuclei evolve on a single BO potential energy surface, approximated by a few body interactions.

Ehrenfest molecular dynamics

To avoid the dimensionality bottleneck the coupled equations:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \langle H_e \rangle \quad (66)$$

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + V_{ne}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \chi(\{\mathbf{R}_I\}, t) \right] \Psi \quad (67)$$

can be solved simultaneously.

The time-dependent Schrodinger equation is solved *on the fly* as the nuclei are propagated using classical mechanics.

Using

$$\Psi(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = \sum_{I=0}^{\infty} c_I(t) \Psi_I(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$$

the Ehrenfest equations reads:

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \sum_k |c_k(t)|^2 E_k \quad (68)$$

$$= -\sum_k |c_k(t)|^2 \nabla_I E_k + \sum_{k,l} c_k^* c_l (E_k - E_l) \mathbf{d}_I^{kl} \quad (69)$$

$$i\hbar \dot{c}_k(t) = c_k(t) E_k - i\hbar \sum_l c_l(t) D^{kl} \quad (70)$$

where the non-adiabatic coupling elements are given by

$$D^{kl} = \int \Psi_k^* \frac{\partial}{\partial t} \Psi_l d\mathbf{r} = \sum_I \dot{\mathbf{R}}_I \int \Psi_k^* \nabla_I \Psi_l = \sum_I \dot{\mathbf{R}}_I \mathbf{d}^{kl}. \quad (71)$$