

Electronic Stopping: Background and Simulation Methods

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Joint ICTP-IAEA Workshop on Non-Adiabatic Dynamics and
Radiation Damage in Nuclear Materials

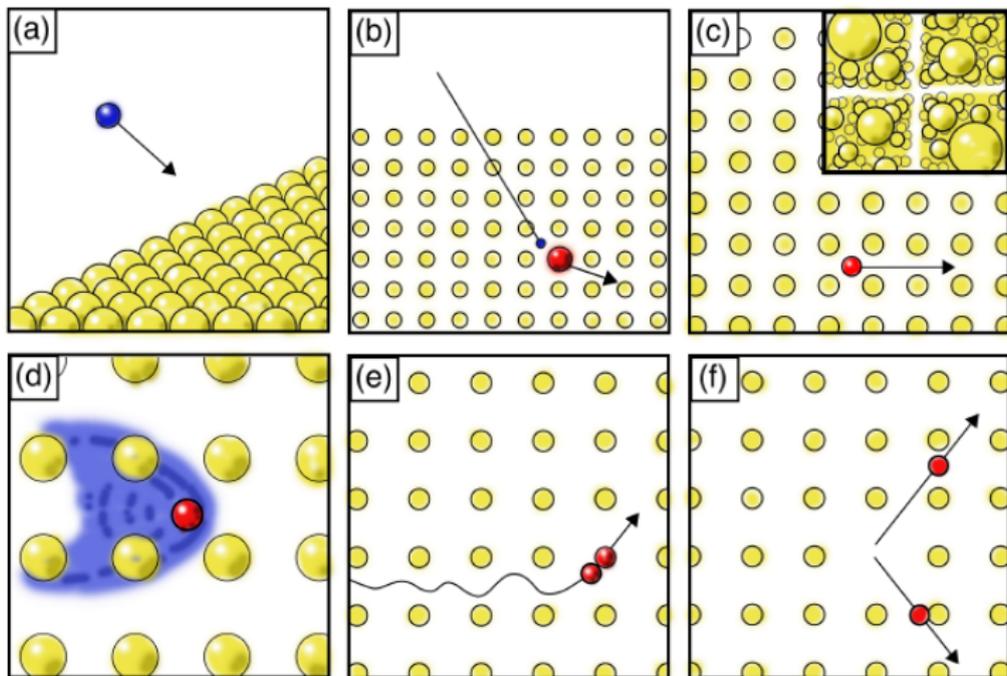


Outline

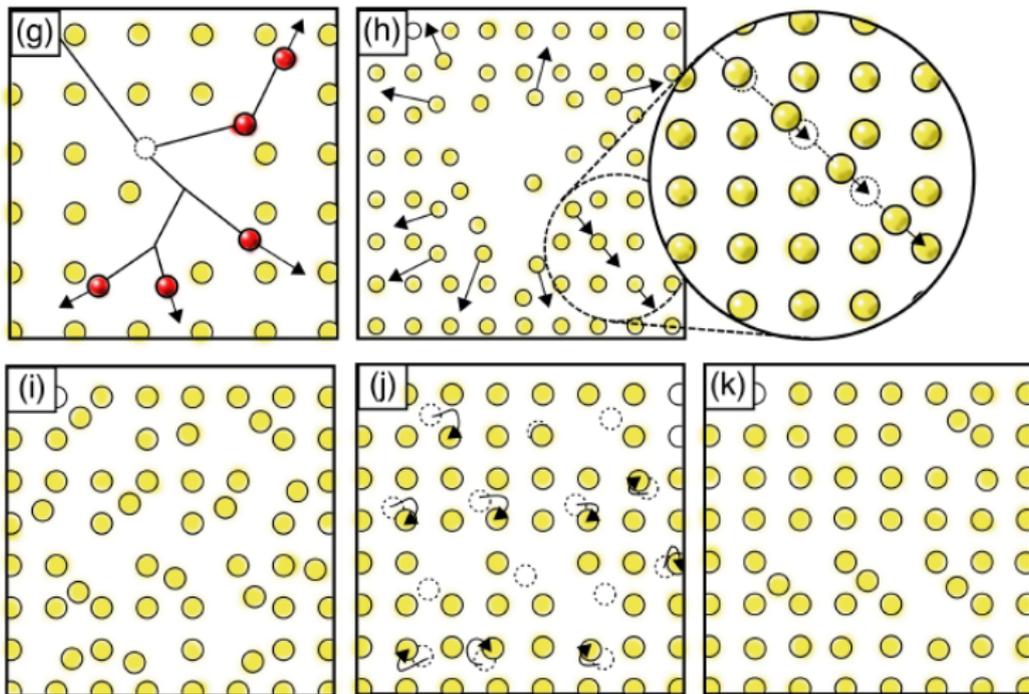
- 1 Electronic Stopping
- 2 Born-Oppenheimer Quantum Molecular Dynamics
- 3 Ehrenfest Quantum Molecular Dynamics

- 1 Electronic Stopping
 - Stopping regimes
 - Fast light ions
 - Slow heavy ions
- 2 Born-Oppenheimer Quantum Molecular Dynamics
- 3 Ehrenfest Quantum Molecular Dynamics

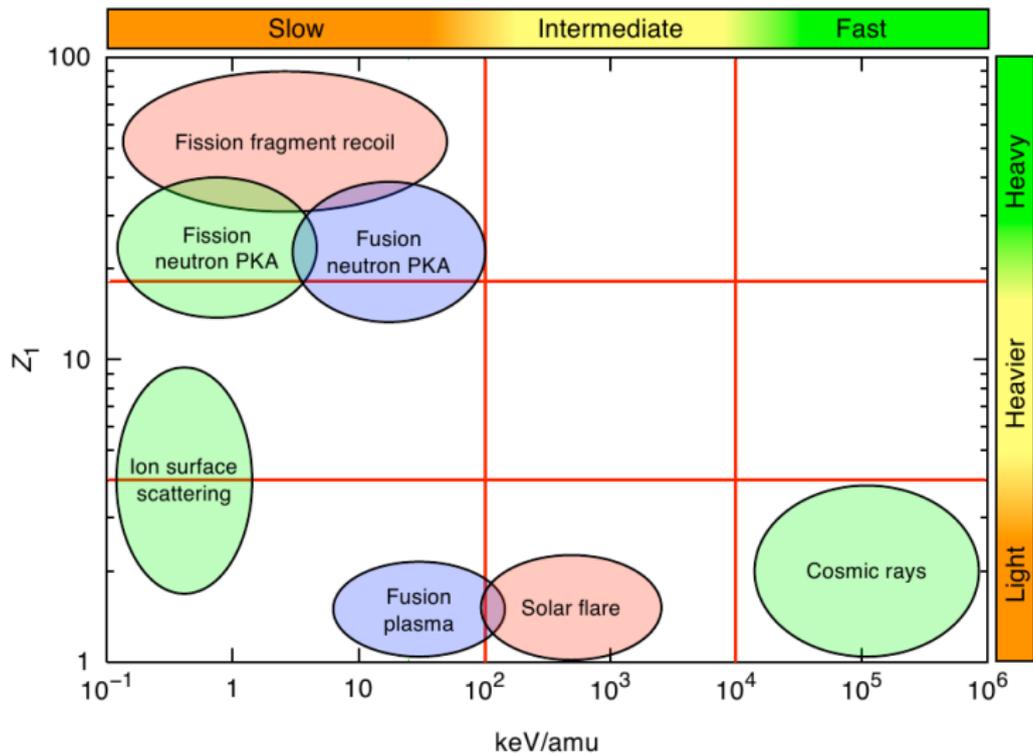
Stopping: Early Stages



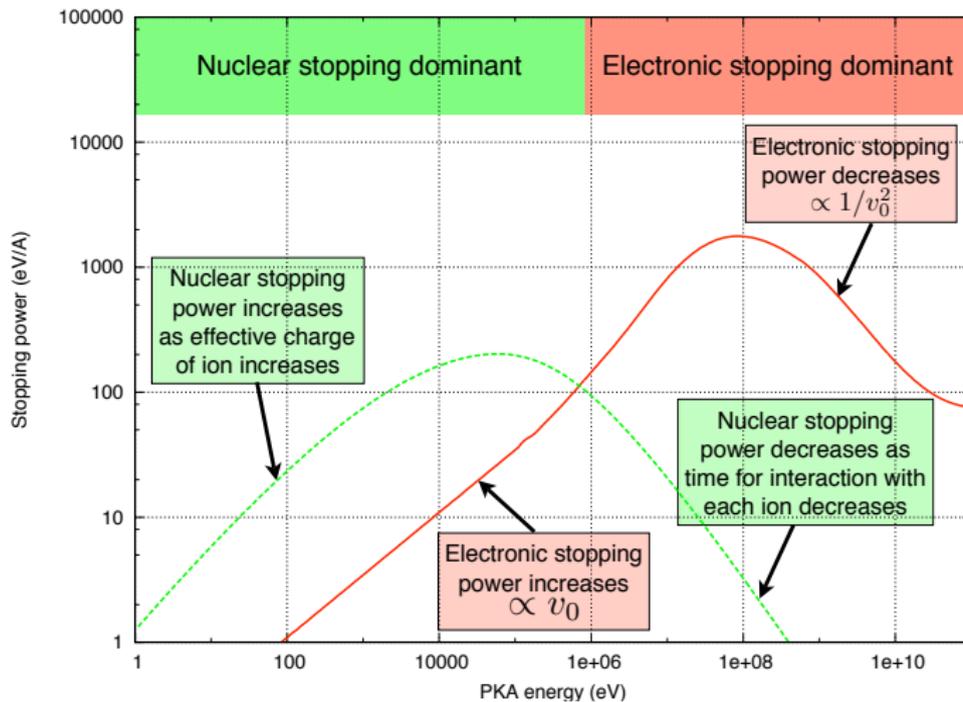
Stopping: Later Stages



Stopping Regimes



Stopping in Fe



Stopping Power

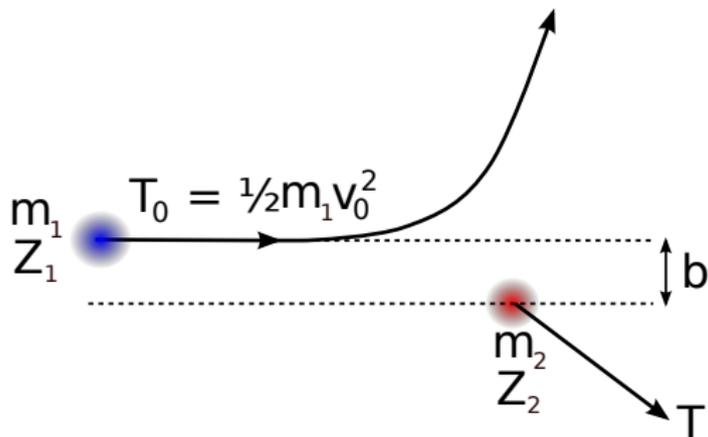
- The **stopping power** is not a power at all. It is the energy lost per unit path length and has the dimensions of a force.
- We are mainly interested in the “low” v_0 regime.

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Fast Light Ions

- Completely stripped of electrons
- Move so fast that they hardly interact with nuclei
- Most energy lost to electrons near path
- Collision approach sensible

Rutherford Scattering



KE of m_2 after collision is

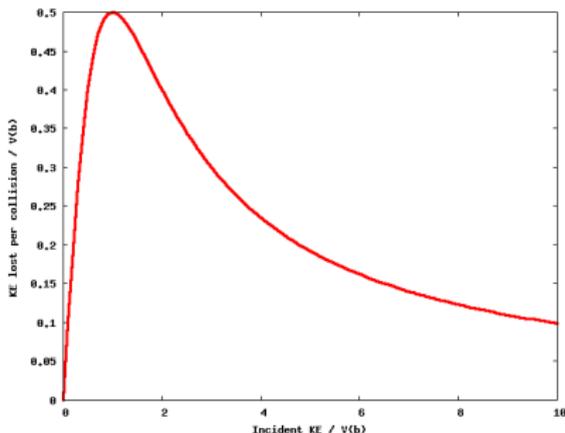
$$T = \frac{4m_1m_2T_0}{(m_1 + m_2)^2 + \left(\frac{2m_2T_0}{V_c(b)}\right)^2}$$

where $V_c(b) = Z_1Z_2e^2/b$.

Ion-Ion Collisions in Fe

If $m_1 = m_2$, Rutherford formula reduces to

$$T = \frac{T_0}{1 + (T_0/V_c(b))^2}$$



For Fe ($Z = 26$, $b \approx 1a_0$), peak occurs at $T_0 = V_c(b) \approx 18\text{keV}$.

Ion-Electron Collisions in Fe

The “shape” of $T(b)$ is much the same when $m_1 \gg m_2$, but the energy scales are very different.

- Assuming $b \approx 1 a_0$, energy lost per collision is maximised when

$$T_0 \approx 35 \text{ MeV}$$

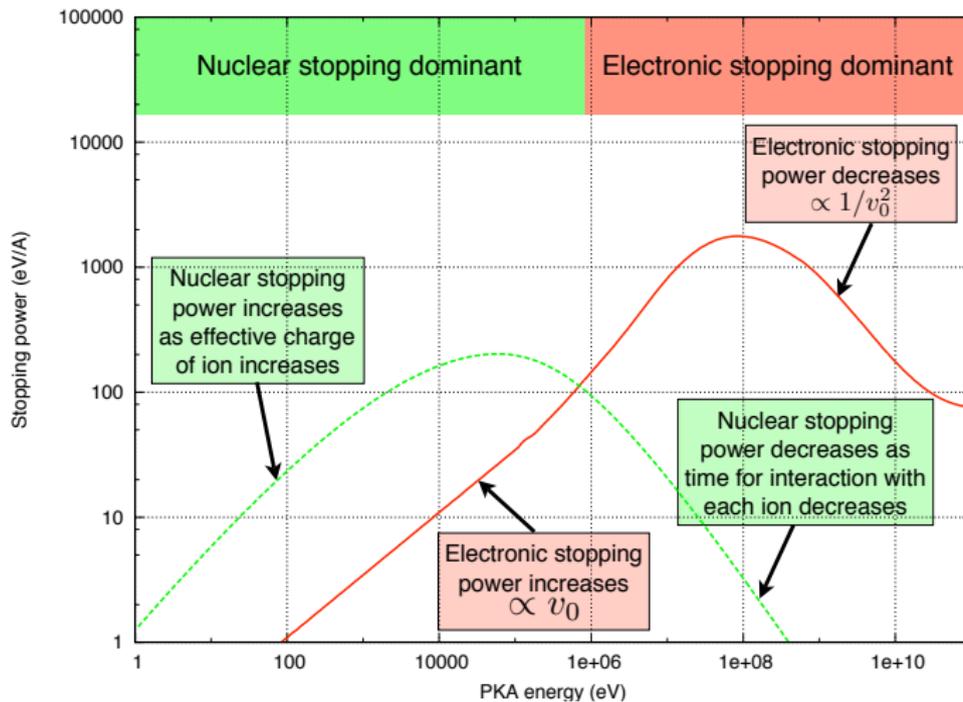
This is **very large**.

- For an Fe ion with $T_0 = 1 \text{ keV}$ ($v_0 \sim 0.027 \text{ a.u.} = 0.027 \hbar/m_e a_0$), maximum energy transferred to electron (head-on collision) is

$$T \approx 40 \text{ meV}$$

This is **very small**.

Stopping in Fe



Electronic Stopping Power at Low and High v_0

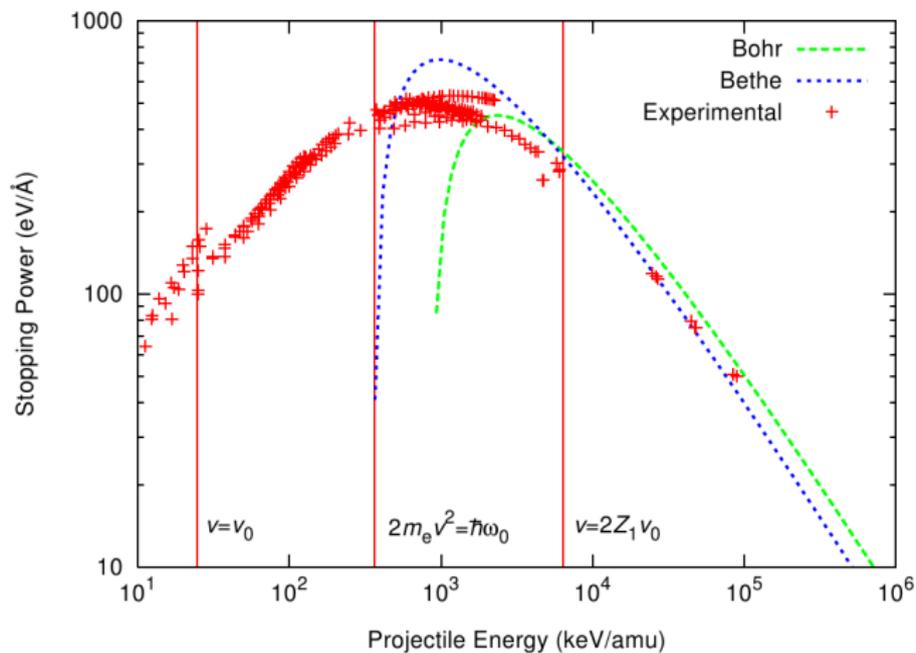
- The **electronic** stopping power is $\propto v_0$ when v_0 is small and $\propto 1/v_0^2$ when v_0 is large.
- The Rutherford formula

$$T = \frac{4m_1 m_2 T_0}{(m_1 + m_2)^2 + \left(\frac{2m_2 T_0}{V_c(b)}\right)^2}$$

predicts that

- $T \approx T_0 \propto v_0^2$ when T_0 is small ✗
- $T \propto 1/T_0 \propto 1/v_0^2$ when T_0 is large ✓

Stopping of O in Au



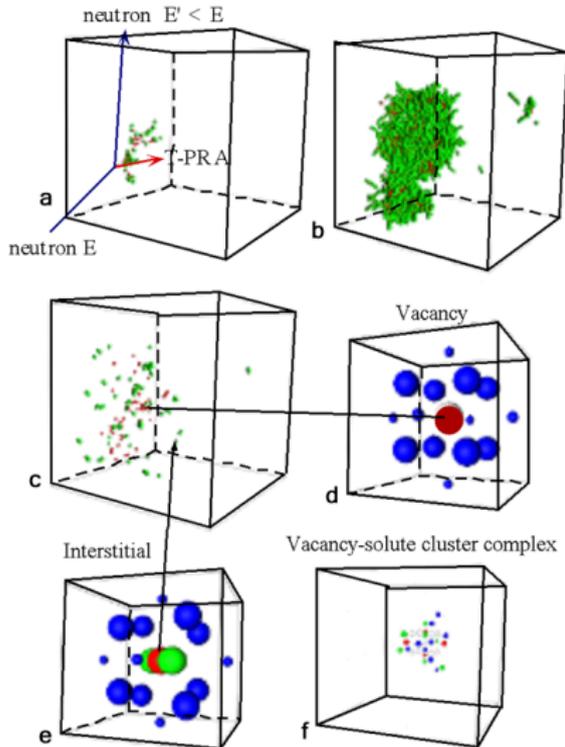
(<http://www.exphys.uni-linz.ac.at/stopping/>)

Limitations of Collision Picture

- Collision idea sensible at high v_0 .
- At low v_0
 - Energy transferred per ion-electron collision is small
 - electrons cannot be regarded as free
 - Fermi statistics and electron density-of-states at E_F matter
 - Electrons act collectively to screen field of moving ion
 - electrons cannot be treated as independent
 - effective ionic charge depends on velocity
 - proper treatment of electronic screening requires QM
 - Ions and electrons of solid respond collectively to moving ion

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Cascade Physics



- ps time scales
- nm length scales
- electronic $T \sim 10^4\text{K}$

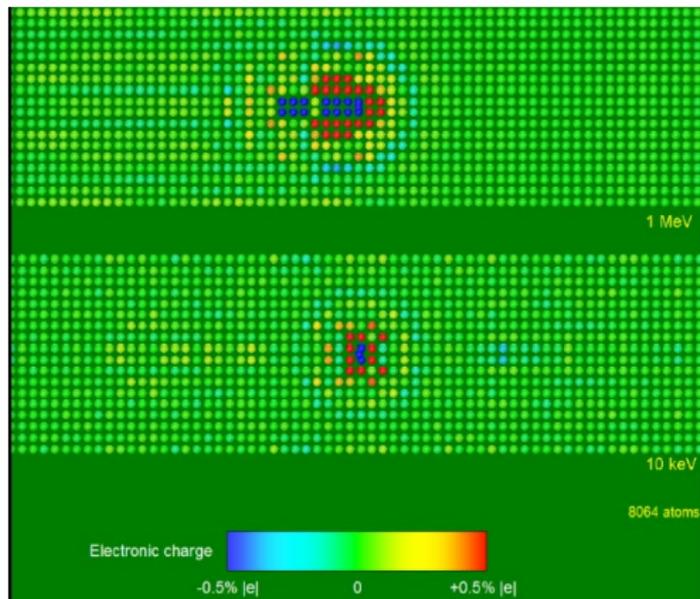
● ~ 100 ps

● hours or days

- Electronic stopping may promote or inhibit defect production:
 - increases rate at which ions lose energy, reducing number of defects formed
 - but also increases cooling rate, quenching in defects
- To understand electronic stopping properly, need QM.
- A distinction is often made between electronic stopping in the displacement phase and the electron-phonon phase, but the border is fuzzy. (We don't find much difference.)

Dynamic Screening

A point charge q moves at velocity \mathbf{v}_0 through a solid.
At high velocity, the electronic screening cloud cannot keep up.



Linear Response Theory

- Apply a weak potential $V_{\text{app}}(\mathbf{r}, t)$ to a uniform electron gas.
- Since the perturbation is weak, the relationship between the applied and screened potentials is linear:

$$V_{\text{scr}}(\mathbf{r}, t) = \int \epsilon^{-1}(|\mathbf{r} - \mathbf{r}'|, t - t') V_{\text{app}}(\mathbf{r}', t') d\mathbf{r}' dt'$$

- This looks much simpler after Fourier transformation:

$$V_{\text{scr}}(\mathbf{k}, \omega) = \epsilon^{-1}(k, \omega) V_{\text{app}}(\mathbf{k}, \omega)$$

The Perturbation

- In our case, the applied Coulomb potential is

$$V_{\text{app}}(\mathbf{r}, t) = \frac{q}{|\mathbf{r} - \mathbf{v}_0 t|}$$

- Fourier transforming gives

$$V_{\text{app}}(\mathbf{k}, \omega) = \frac{8\pi^2 q}{k^2} \delta(\mathbf{v}_0 \cdot \mathbf{k} - \omega)$$

Linear Response Calculation (cont.)

- Assuming that the perturbation is weak (which it is not), we can find the screened potential via

$$V_{\text{scr}}(\mathbf{k}, \omega) = \varepsilon^{-1}(k, \omega) V_{\text{app}}(\mathbf{k}, \omega)$$

and then obtain the drag force via

$$\mathbf{F}_{\text{drag}} = -q \nabla V_{\text{scr}}(\mathbf{r}, t)|_{\mathbf{r}=\mathbf{v}_0 t}$$

- Using the Lindhard dielectric function for an electron gas gives

$$\begin{array}{llll} \mathbf{F}_{\text{drag}} \propto v_0 & & v_0 \ll v_F & \checkmark \\ \mathbf{F}_{\text{drag}} \propto 1/v_0^2 & & v_0 \gg v_F & \checkmark \end{array}$$

Limitations of Screening Approach

- Perturbation is **not weak**.
- Solids are **not uniform**. Drag force should depend on position and direction of motion of ion.
- **No chemistry**. Electronic stopping in insulators differs drastically from electronic stopping in metals.

Electronic Stopping at Low Energy

- Our work . . .
 - Investigate electronic stopping at low v_0 using quantum MD simulations.
 - Requires us to go beyond the Born-Oppenheimer approximation.

Instead of standard quantum MD, we use
Ehrenfest Dynamics

- Goals
 - We cannot (yet) simulate a full cascade using QM.
 - Can QM help us work out how to incorporate electronic stopping into MD simulations?

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The Schrödinger Equation for a Solid

$$\left[\sum_a \left(-\frac{1}{2M} \nabla_{\mathbf{R}_a}^2 \right) + \sum_i \left(-\frac{1}{2} \nabla_{\mathbf{r}_i}^2 \right) - \sum_i \sum_a \frac{Z_a e^2}{|\mathbf{r}_i - \mathbf{R}_a|} + \frac{1}{2} \sum_i \sum_{j (\neq i)} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_a \sum_{b (\neq a)} \frac{Z_a Z_b e^2}{|\mathbf{R}_a - \mathbf{R}_b|} \right] \psi = i \frac{\partial \psi}{\partial t}$$

where

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, t)$$

is far too complicated to write out repeatedly.

- Define

- $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$

- $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_I})$

- $\nabla_{\mathbf{r}} = (\nabla_{\mathbf{r}_1}, \nabla_{\mathbf{r}_2}, \dots, \nabla_{\mathbf{r}_N})$

- $\nabla_{\mathbf{R}} = (\nabla_{\mathbf{R}_1}, \nabla_{\mathbf{R}_2}, \dots, \nabla_{\mathbf{R}_{N_I}})$

- Define

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- $\nabla_{\mathbf{r}} = (\nabla_{\mathbf{r}_1}, \nabla_{\mathbf{r}_2}, \dots, \nabla_{\mathbf{r}_N})$
- $\nabla_{\mathbf{R}} = (\nabla_{\mathbf{R}_1}, \nabla_{\mathbf{R}_2}, \dots, \nabla_{\mathbf{R}_{N_f}})$

- Then we can use the simpler notation

Schrödinger Equation for a Solid

$$\left[-\frac{1}{2M} \nabla_{\mathbf{R}}^2 - \frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \psi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial \psi(\mathbf{r}, \mathbf{R}, t)}{\partial t}$$

- Define

- $\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$
- $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_f})$
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Schrödinger Equation for a Solid

$$\left[-\frac{1}{2M} \nabla_{\mathbf{R}}^2 - \frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \psi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial \psi(\mathbf{r}, \mathbf{R}, t)}{\partial t}$$

The central mathematical problem of electronic structure theory is to solve the Schrödinger equation to discover the properties of materials.

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The Born-Oppenheimer Approximation

The Schrödinger equation for a solid or large molecule

$$\left[-\frac{1}{2M} \nabla_{\mathbf{R}}^2 - \frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \Psi(\mathbf{r}, \mathbf{R}, t) = i \frac{\partial \Psi(\mathbf{r}, \mathbf{R}, t)}{\partial t}$$

is so intractable that we must approximate.

- The nuclear mass is large, so the nuclei move slowly and their wave packets are typically only 1/20 of the inter-atomic spacing in size.
- From the point of view of the electrons, the nuclei are **almost stationary** and **almost point-like**.

The electronic Hamiltonian

- This suggests that it might be useful to solve the electronic Schrödinger equation

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \phi_i(\mathbf{r}; \mathbf{R}) = E_i(\mathbf{R}) \phi_i(\mathbf{r}; \mathbf{R})$$

to find the electronic eigenfunctions $\phi_i(\mathbf{r}; \mathbf{R})$ and eigenvalues $E_i(\mathbf{R})$ for a fixed set of nuclear positions \mathbf{R} .

- The nuclei are being treated as fixed point-like particles. The nuclear KE term has been omitted.
- The electronic eigenstates $\phi_i(\mathbf{r}; \mathbf{R})$ are best regarded as functions of \mathbf{r} only. The *forms* of those functions depend parametrically on the frozen nuclear positions \mathbf{R} .

The electronic eigenfunctions as a basis

- For any specific choice of \mathbf{R} , the electronic eigenfunctions $\Phi_j(\mathbf{r}; \mathbf{R})$ are a complete orthonormal basis for functions of \mathbf{r} . Thus, it must be possible to expand the full many-electron wave function $\Psi(\mathbf{r}, \mathbf{R}, t)$ in the form

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j \chi_j(\mathbf{R}, t) \Phi_j(\mathbf{r}; \mathbf{R}) .$$

- The expansion coefficients $\chi_j(\mathbf{R}, t)$ depend on time t and nuclear position \mathbf{R} . They need *not* all have the same normalisation.

The Born-Oppenheimer approximation

The BO approximation assumes that a single term (usually the ground state) dominates this expansion:

$$\Psi(\mathbf{r}, \mathbf{R}, t) \approx \chi_0(\mathbf{R}, t)\Phi_0(\mathbf{r}; \mathbf{R})$$

- The electrons follow the ground electronic state $\Phi_0(\mathbf{r}; \mathbf{R})$ **adiabatically** as the nuclei move (slowly) around.
- Given this assumption, it can be shown that the evolution of the nuclear wavefunction is given approximately by a Schrödinger-like equation

$$\left[-\frac{1}{2M} \nabla_{\mathbf{R}}^2 + E_0(\mathbf{R}) \right] \chi_0(\mathbf{R}, t) = i \frac{\partial \chi_0(\mathbf{R}, t)}{\partial t}$$

in which the ground-state electronic eigenvalue $E_0(\mathbf{R})$ appears as a **potential**.

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Time Derivatives of Expectation Values

$$\hat{H}(t)\psi = i\frac{\partial\psi}{\partial t}$$

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- $$\frac{d\langle\psi|\hat{O}|\psi\rangle}{dt} = \langle\frac{\partial\psi}{\partial t}|\hat{O}|\psi\rangle + \langle\psi|\hat{O}|\frac{\partial\psi}{\partial t}\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle$$

Time Derivatives of Expectation Values

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- $$\begin{aligned}\frac{d\langle\psi|\hat{O}|\psi\rangle}{dt} &= \left\langle\frac{\partial\psi}{\partial t}|\hat{O}|\psi\right\rangle + \langle\psi|\hat{O}|\frac{\partial\psi}{\partial t}\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle \\ &= \langle(-i\hat{H}\psi)|\hat{O}|\psi\rangle + \langle\psi|\hat{O}|(-i\hat{H}\psi)\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle\end{aligned}$$

Time Derivatives of Expectation Values

$$\hat{H}(t)\psi = i\frac{\partial\psi}{\partial t}$$

- $$\begin{aligned}\frac{d\langle\psi|\hat{O}|\psi\rangle}{dt} &= \left\langle\frac{\partial\psi}{\partial t}|\hat{O}|\psi\right\rangle + \langle\psi|\hat{O}|\frac{\partial\psi}{\partial t}\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle \\ &= \langle(-i\hat{H}\psi)|\hat{O}|\psi\rangle + \langle\psi|\hat{O}|(-i\hat{H}\psi)\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle \\ &= i\langle\psi|[\hat{H}, \hat{O}]|\psi\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle\end{aligned}$$

Time Derivatives of Expectation Values

$$\hat{H}(t)\psi = i\frac{\partial\psi}{\partial t}$$

- $$\begin{aligned}\frac{d\langle\psi|\hat{O}|\psi\rangle}{dt} &= \left\langle\frac{\partial\psi}{\partial t}|\hat{O}|\psi\right\rangle + \langle\psi|\hat{O}|\frac{\partial\psi}{\partial t}\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle \\ &= \langle(-i\hat{H}\psi)|\hat{O}|\psi\rangle + \langle\psi|\hat{O}|(-i\hat{H}\psi)\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle \\ &= i\langle\psi|[\hat{H}, \hat{O}]|\psi\rangle + \langle\psi|\frac{d\hat{O}}{dt}|\psi\rangle\end{aligned}$$

- If $\hat{O} = \hat{H}$, obtain

$$\frac{d\langle\psi|\hat{H}|\psi\rangle}{dt} = \langle\psi|\frac{d\hat{H}}{dt}|\psi\rangle$$

The Ehrenfest Equations

The Hamiltonian for the Born-Oppenheimer nuclear wave function χ_0 is

$$\hat{H} = -\frac{1}{2M}\nabla_{\mathbf{R}}^2 + E_0(\mathbf{R})$$

Hence

$$\frac{d\bar{\mathbf{R}}}{dt} = i\langle\chi_0|[\hat{H}, \hat{\mathbf{R}}]|\chi_0\rangle = \langle\chi_0|\left(\frac{-i\nabla_{\mathbf{R}}}{M}\right)|\chi_0\rangle = \bar{\mathbf{P}}/M$$

$$\frac{d\bar{\mathbf{P}}}{dt} = i\langle\chi_0|[\hat{H}, \hat{\mathbf{P}}]|\chi_0\rangle = \langle\chi_0|(-\nabla_{\mathbf{R}}E_0(\mathbf{R}))|\chi_0\rangle = \bar{\mathbf{F}}$$

If the nuclear wavefunctions are narrow and remain narrow (in position and momentum), we can follow their centroids by solving **Newton's laws** with $E_0(\mathbf{R})$ as the potential!

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Quantum Molecular Dynamics

We now have all of the ingredients required for a quantum MD simulation.

- The electronic Schrödinger equation

$$\left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right] \Phi_0(\mathbf{r}; \mathbf{R}) = E_0(\mathbf{R}) \Phi_0(\mathbf{r}; \mathbf{R})$$

is solved to find the ground-state electronic energy surface $E_0(\mathbf{R})$. (In practice this is done approximately using ground state DFT.)

- The nuclei move according to Newton's laws:

$$M \frac{d^2 \mathbf{R}}{dt^2} = -\nabla_{\mathbf{R}} E_0(\mathbf{R}) .$$

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 - Failure of the Born-Oppenheimer approximation
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Failure of the Born-Oppenheimer Approximation

- In Born-Oppenheimer quantum MD, the nuclei move according to Newton's 2nd law

$$M \frac{d^2 \mathbf{R}}{dt^2} = -\nabla_{\mathbf{R}} E_0(\mathbf{R})$$

- The potential $E_0(\mathbf{R})$ depends only on the current nuclear positions, so the nuclear motion is **conservative**.

There is no electronic drag

How the Born-Oppenheimer Approximation Fails

- The Born-Oppenheimer approximation assumes that

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \chi_0(\mathbf{R}, t)\Phi_0(\mathbf{r}; \mathbf{R})$$

- In reality, even if Ψ has this form at $t=0$, the time evolution introduces contributions from other electronic eigenstates

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j \chi_j(\mathbf{R}, t)\Phi_j(\mathbf{r}; \mathbf{R})$$

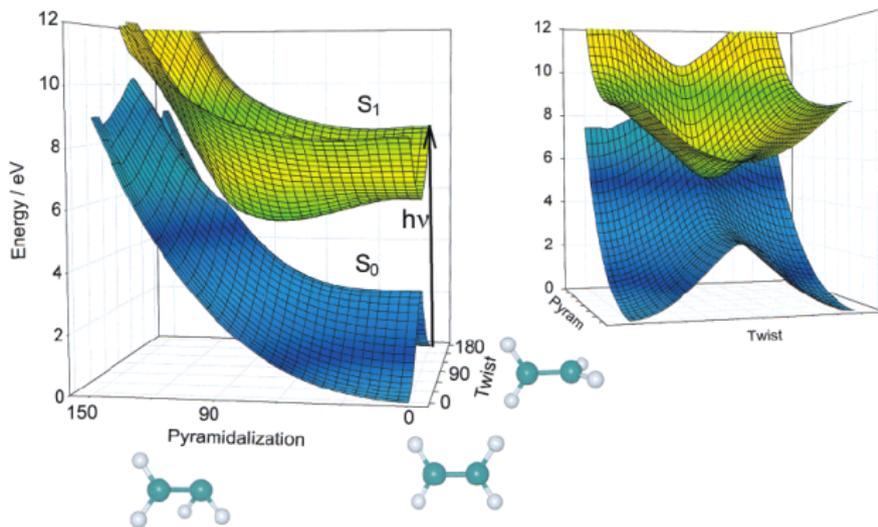
- The electronic excitations are created at the expense of nuclear KE, slowing the nuclei \Rightarrow drag.

When the Born-Oppenheimer Approximation Fails

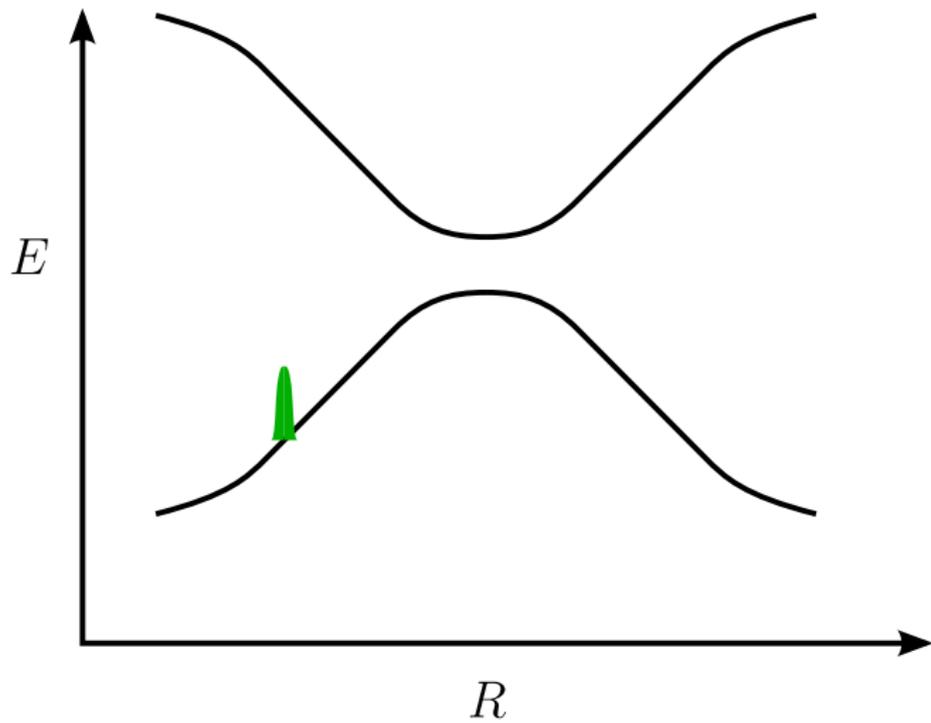
- The potential of the moving nuclei acts like a time-dependent perturbation applied to the electronic system. The nuclei move slowly, so $\hbar\omega$ is normally much smaller than $E_i(\mathbf{R}) - E_j(\mathbf{R})$.
- If the nuclear wavepacket moves to a region where $E_i(\mathbf{R})$ and $E_j(\mathbf{R})$ are very close, so that $|E_j(\mathbf{R}) - E_i(\mathbf{R})| \approx \hbar\omega$, the electronic system may make transitions.

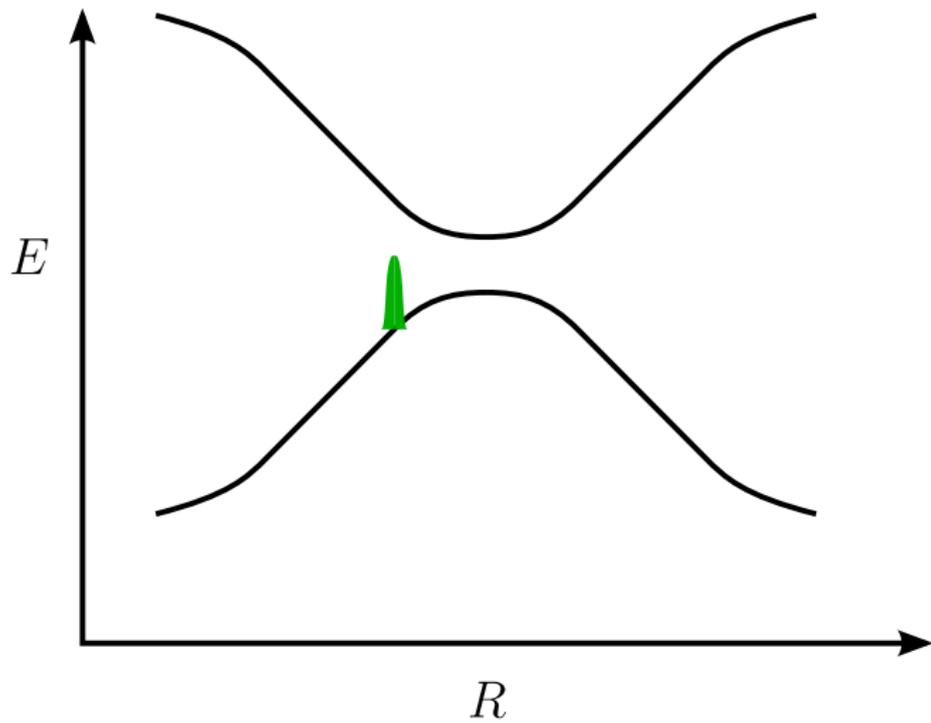
The Born-Oppenheimer approximation fails where

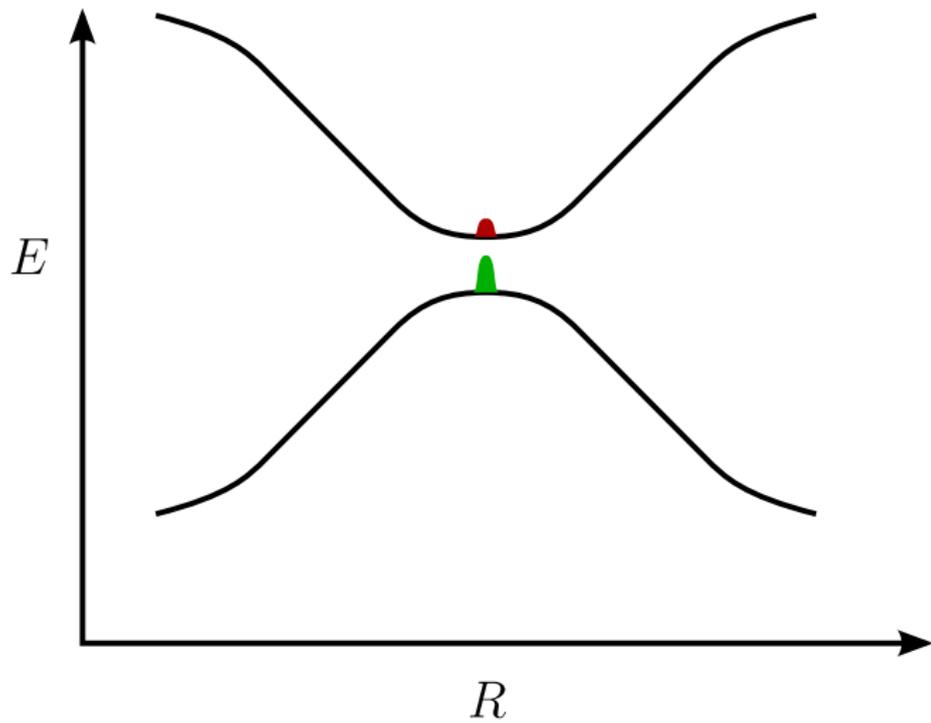
$$E_i(\mathbf{R}) \approx E_j(\mathbf{R})$$

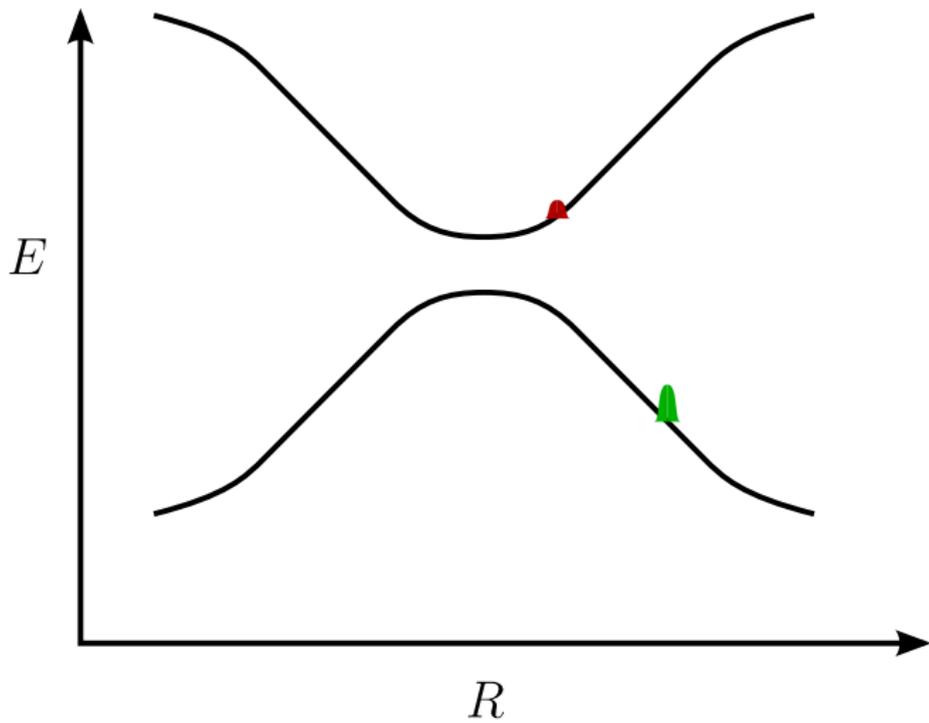


Ground and first excited-state Born-Oppenheimer surfaces of ethylene









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The Ehrenfest Approximation

- To model electronic friction, we must allow the motion of the nuclei to create electronic excitations.
- In the Ehrenfest approximation, the electronic wave function $\Psi(\mathbf{r}, t)$ evolves according to a **time-dependent** Schrödinger equation

$$\left[-\frac{1}{2m} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}(t)) \right] \Phi(\mathbf{r}, t) = i \frac{\partial \Phi(\mathbf{r}, t)}{\partial t}$$

- The potential felt by the electrons depends on the positions of the classical nuclei and changes as the ions move.
 - If the ions move fast, electronic excitations are created. The electrons are not quenched back to their ground state and the nuclei slow down \Rightarrow drag.

The Ehrenfest Approximation (cont.)

- The ions evolve according to Newton's laws under the influence of forces from the other ions *and* the electrons

$$\frac{d\mathbf{R}}{dt} = \frac{\mathbf{P}}{M} \quad \frac{d\mathbf{P}}{dt} = \int \Phi^* (-\nabla_{\mathbf{R}} V) \Phi \, d\mathbf{r}$$

- The total classical+quantum energy

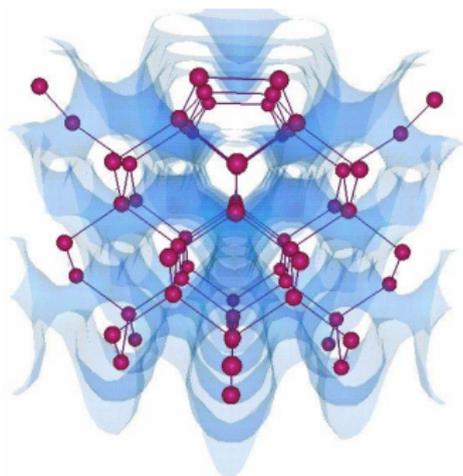
$$\frac{P^2}{2M} + \int \Phi \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right) \Phi \, d\mathbf{r}$$

is conserved.

Ehrenfest Force on a Nucleus

$$\begin{aligned}\frac{d\mathbf{P}_a}{dt} &= \int \Phi^*(\mathbf{r}) \left[-\nabla_{\mathbf{R}_a} V(\mathbf{r}, \mathbf{R}) \right] \Phi(\mathbf{r}) d\mathbf{r} \\ &= (Z_a e) \left[\mathcal{E}^{\text{ionic}}(\mathbf{R}_a) + \mathcal{E}^{\text{electronic}}(\mathbf{R}_a) \right]\end{aligned}$$

The nuclei feel electrostatic forces from the other nuclei and from the electronic charge density. This seems very natural.



Ehrenfest Energy Conservation

- The Ehrenfest energy is

$$E = \frac{P^2}{2M} + \langle \Phi | \hat{H}_{\text{Ehr}}(t) | \Phi \rangle$$

where $\hat{H}_{\text{Ehr}}(t) = -\frac{1}{2}\nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}(t))$.

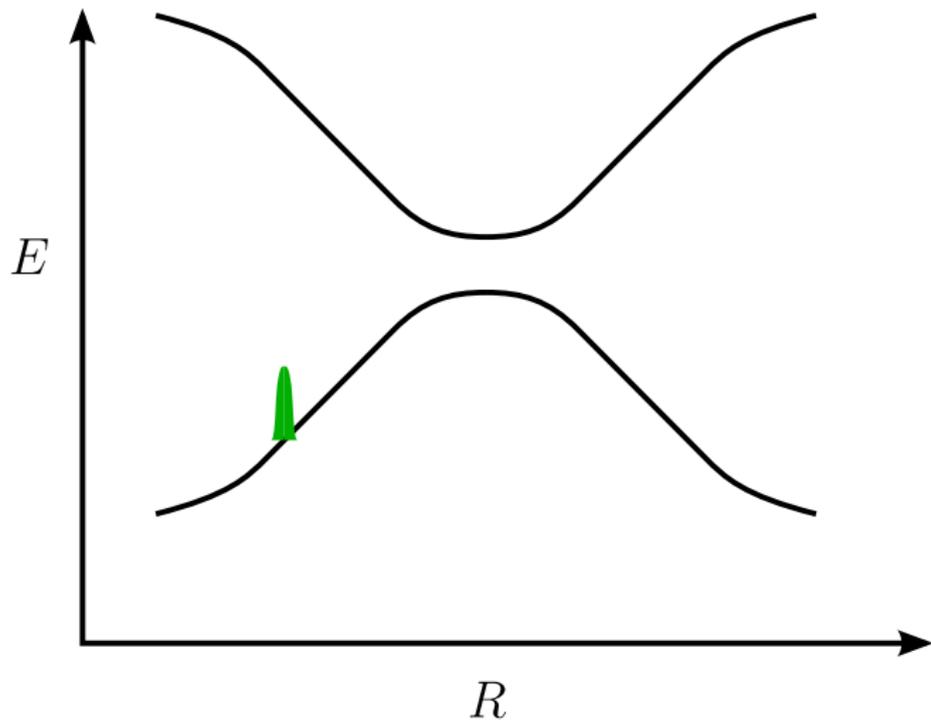
- Hence

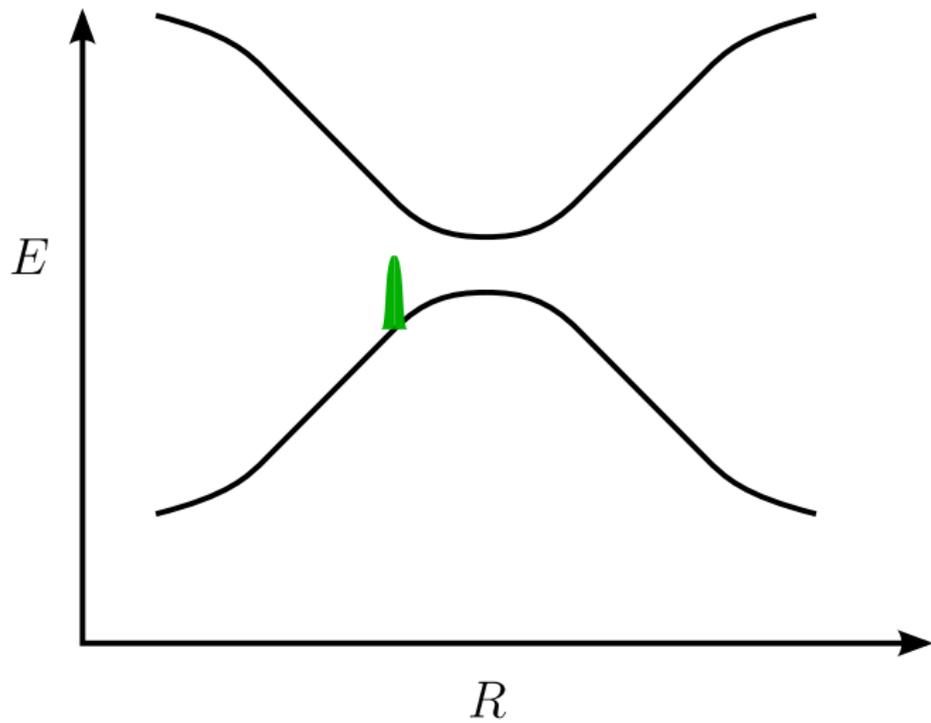
$$\begin{aligned} \frac{dE}{dt} &= \left(\frac{\mathbf{P}}{M} \right) \cdot \left(\frac{d\mathbf{P}}{dt} \right) + \langle \Phi | \frac{d\hat{H}_{\text{Ehr}}}{dt} | \Phi \rangle \\ &= \dot{\mathbf{R}} \cdot \langle \Phi | (-\nabla_{\mathbf{R}} V) | \Phi \rangle + \langle \Phi | (\dot{\mathbf{R}} \cdot \nabla_{\mathbf{R}} V) | \Phi \rangle \\ &= 0 \end{aligned}$$

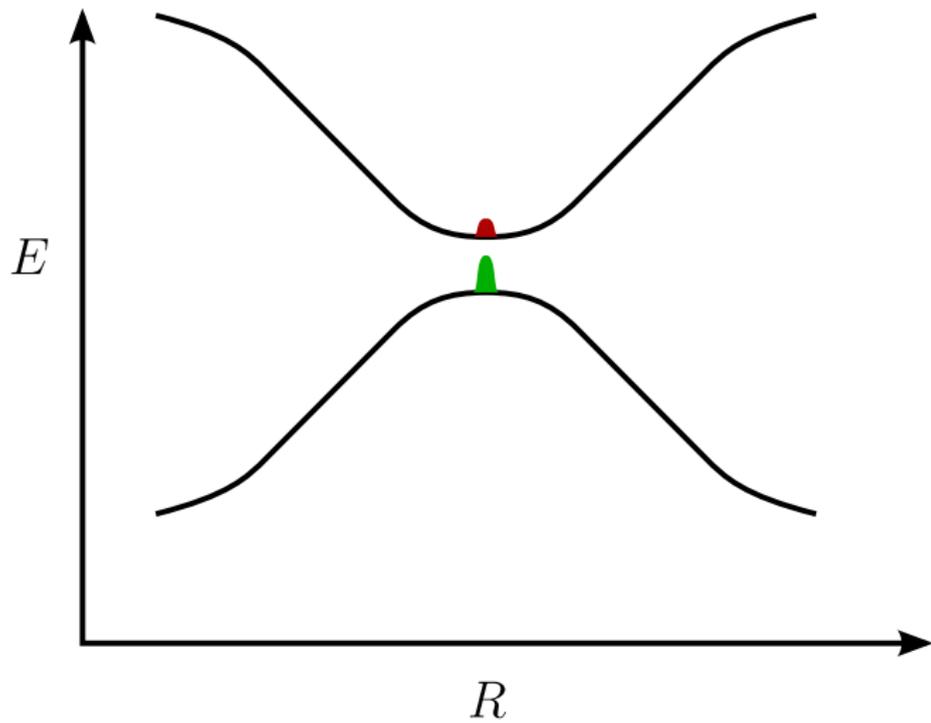
- If you believe that the ions are point-like and classical, the Ehrenfest approximation seems a natural way to allow electronic excitations to take place:

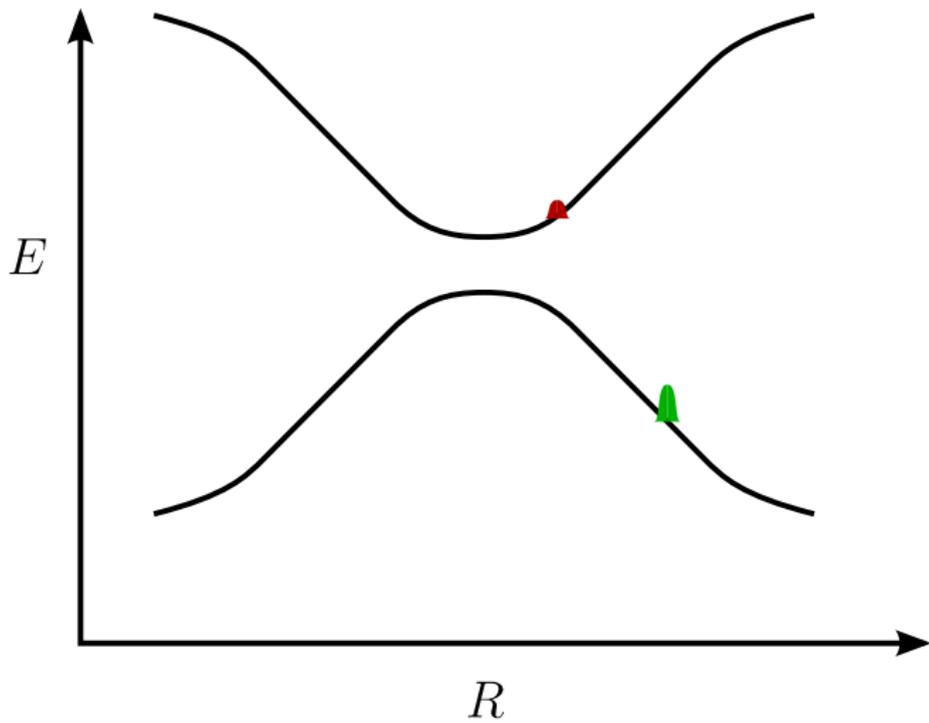
$$\chi_0(\mathbf{R}, t)\Phi_0(\mathbf{r}; \mathbf{R}) \longrightarrow \sum_j \chi_j(\mathbf{R}, t)\Phi_j(\mathbf{r}; \mathbf{R})$$

- But remember what happens at a conical intersection ...









Limitations (cont.)

The nuclear wavepacket splits into disjoint pieces propagating at different speeds.

- In low-energy molecular chemistry, the Ehrenfest approximation is often unreliable. Quantum chemists do not like it.
- In radiation damage simulations, as will be explained in tomorrow's lecture, it seems to be OK as long as the ions are moving fast.

- 1 Electronic Stopping
- 2 Born-Oppenheimer Quantum Molecular Dynamics
- 3 Ehrenfest Quantum Molecular Dynamics
 - Failure of the Born-Oppenheimer approximation
 - The Ehrenfest approximation
 - Time-dependent density functional theory

The Role of the Electron Density

- The remaining difficulty is that it is impossible to solve the many-electron Schrödinger equation accurately for any but the smallest systems.
- However, in Ehrenfest dynamics, the electronic wave functions are used only to calculate the electronic parts of the forces on the ions

$$\begin{aligned}\mathbf{F}_a^{\text{electronic}} &= (Z_a e) \mathcal{E}^{\text{electronic}}(\mathbf{R}_a, t) \\ &= (Z_\alpha e) \left(-\nabla_{\mathbf{R}_\alpha} \int \frac{\rho(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{R}_\alpha|} d^3r \right)\end{aligned}$$

Only the electronic charge density is required!

Time-Dependent Density Functional Theory

- The Runge-Gross theorem of TDDFT says that $\rho(\mathbf{r}, t)$ for the interacting system can be obtained *exactly* by solving a time-dependent **non-interacting** problem with an effective potential $V_{\text{eff}}(\mathbf{r}, [\rho], t)$:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}([\rho], \mathbf{r}, t) \right] \psi_i(\mathbf{r}, t) = i \frac{\partial \psi_i(\mathbf{r}, t)}{\partial t}$$
$$\rho(\mathbf{r}, t) = -e \sum_{i \text{ occ}} |\psi_i(\mathbf{r}, t)|^2$$

- The effective potential is density and history-dependent (and nasty), but reasonable approximations exist.

- Time-dependent **one-electron** Schrödinger equations can be solved on computers.
- By combining the Ehrenfest approximation and TDDFT, we obtain a practical method for simulations of radiation damage.

Many-Electron Ehrenfest Dynamics

In many-electron Ehrenfest dynamics, the conserved total energy is

$$\frac{P^2}{2M} + \int \Phi \left(-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}) \right) \Phi \, d\mathbf{r}$$

and the equations of motion are

$$i \frac{\partial \Phi}{\partial t} = \left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V(\mathbf{r}, \mathbf{R}(t)) \right] \Phi$$
$$\frac{d\mathbf{P}}{dt} = \int \Phi^* (-\nabla_{\mathbf{R}} V) \Phi \, d\mathbf{r}$$

TDDFT Ehrenfest Dynamics

In TDDFT Ehrenfest dynamics (at the ALDA level), the conserved total energy is

$$\frac{P^2}{2M} + \sum_{i \text{ occ}} \int \psi_i^* \left(-\frac{1}{2} \nabla^2 \right) \psi_i d^3r + \int V_n \rho d^3r + E_H[\rho] + E_{xc}[\rho] + E_{nn}$$

and the equations of motion are

$$\begin{aligned} i \frac{\partial \psi_i}{\partial t} &= \left[-\frac{1}{2} \nabla_{\mathbf{r}}^2 + V_n(\mathbf{r}) + V_H([\rho], \mathbf{r}) + V_{xc}([\rho], \mathbf{r}) \right] \psi_i \\ \frac{dP}{dt} &= \sum_{i \text{ occ}} \int \psi_i^* (-\nabla_{\mathbf{R}} V_n) \psi_i d^3r - \nabla_{\mathbf{R}} E_{nn} \\ &= \int (-\nabla_{\mathbf{R}} V_n) \rho d^3r - \nabla_{\mathbf{R}} E_{nn} \end{aligned}$$

Status of TDDFT

- TDDFT is a way of solving the many-electron Schrödinger equation with a time-dependent external potential.
- When TDDFT is applied to systems of ions and electrons, the ions are treated as moving classical point charges that exert a time-dependent external potential on the QM electrons.

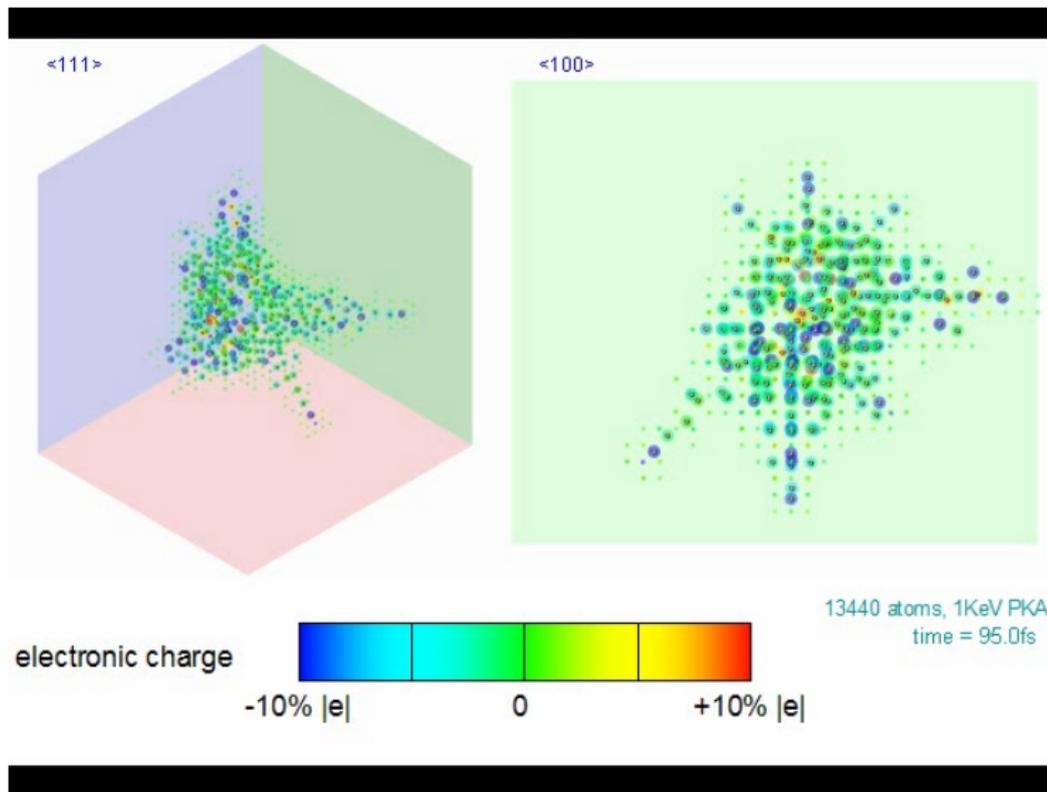
TDDFT simulations of coupled electron-ion systems **always** assume the Ehrenfest approximation

- The Ehrenfest approximation is unreliable in small molecules and when ionic kinetic energies are low.

Practical Considerations

- Large systems ($> 10^4$ atoms) are required:
 - High-energy (MeV) cascade simulations obviously require many atoms.
 - Low-energy (keV) cascades lead to small ion \rightarrow electron energy transfers ($\sim 40\text{meV}$), so the spectrum of electronic excitations must be **very dense**. Again large systems are required.
- Ehrenfest/TDDFT is the future, but further approximations are necessary at present.
- We use a very simple semi-empirical s-band tight-binding Hamiltonian.

QM Cascade Simulation



Conclusions

- TDDFT Ehrenfest simulations will provide a quantitative description of electronic stopping during collision cascades — but we cannot yet simulate large enough systems.
- Semi-empirical TB Ehrenfest simulations include most of the right physics, give useful qualitative results, and can be done today.