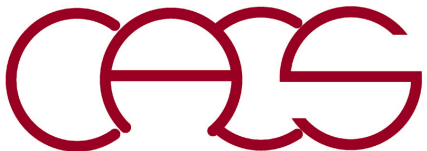


Quantum Molecular Dynamics Basics

Aiichiro Nakano

*Collaboratory for Advanced Computing & Simulations
Depts. of Computer Science, Physics & Astronomy, Chemical
Engineering & Materials Science, and Biological Sciences
University of Southern California*

Email: anakano@usc.edu



Objective

- Derive quantum molecular dynamics (QMD) equations, which follow classical-mechanical trajectories of atoms, while computing interatomic interactions quantum mechanically:

1. Ehrenfest molecular dynamics (EMD)

- Solves the time-dependent Schrödinger equation for electrons
- Attosecond (10^{-18} s) to femtosecond (10^{-15} s) electron dynamics

P. Ehrenfest, *Zeit. Phys.* **45**, 455 ('27)

2. Born-Oppenheimer molecular dynamics (BOMD)

- Obtain the electronic ground state at every time instance
- Electron & nucleus dynamics above femtosecond (10^{-15} s)

M. Born & R. Oppenheimer, *Annal. Phys.* **84**, 457 ('27)



Paul Ehrenfest
(1880-1933)



Max Born
(1882-1970)



Robert Oppenheimer
(1904-1967)

Electron-Nucleus Dynamics

- Consider a system of N electrons & N_{atom} nuclei, with their position operators, $\{\mathbf{r}_i | i = 1, \dots, N\}$ & $\{\mathbf{R}_I | I = 1, \dots, N_{\text{atom}}\}$

$$\begin{aligned}
 H &= \sum_{I=1}^{N_{\text{atom}}} \frac{\mathbf{P}_I^2}{2M_I} + h(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) \\
 &= \sum_{I=1}^{N_{\text{atom}}} \left[\frac{\mathbf{P}_I^2}{2M_I} + V_{\text{ext}}(\mathbf{R}_I) \right] + \sum_{i=1}^N \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{ext}}(\mathbf{r}_i) \right] \\
 &\quad + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,J} \frac{Z_J e^2}{|\mathbf{r}_i - \mathbf{R}_J|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} \\
 &\quad \text{electron-electron interaction} \quad \text{electron-nuclei interaction} \quad \text{nuclei-nuclei interaction}
 \end{aligned}$$

- Here, \hbar is the Planck constant, \mathbf{P}_I , M_I & Z_I are the momentum, mass & charge of the I -th nucleus, and m & e are the electron mass & charge; V_{ext} & v_{ext} are external potentials (like external electric field) acting on nuclei & electrons, respectively
- We focus on the system dynamics described by the time-dependent Schrödinger equation in non-relativistic quantum mechanics, where $\Psi_{\text{e+n}}$ is the electron-nucleus wave function & t is the time

$$i\hbar \frac{\partial}{\partial t} \Psi_{\text{e+n}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t) = H \Psi_{\text{e+n}}(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}, t)$$

Separation of Length Scales

- Due to the much larger nuclei masses (M_I) compared to the electron mass (m), the quantum-mechanical nature of nuclei is negligible except in extreme cases like nuclear fusion
- More specifically, the length scale below which a particle's quantum-mechanical nature becomes appreciable at a given temperature T (*i.e.*, thermal de Broglie wave length) is much smaller for nuclei than for electron

$$\Lambda_I = \frac{\hbar}{\sqrt{2\pi M_I k_B T}} \ll \underbrace{\lambda}_{\text{length scale of interest in QMD}} \sim \Lambda_{\text{electron}} = \frac{\hbar}{\sqrt{2\pi m k_B T}}$$

Element	Λ (a.u.) at 300 K
electron	12.94
proton	0.302
C	8.72×10^{-2}
O	7.55×10^{-2}
Zn	3.74×10^{-2}

1 a.u. (bohr) = 0.529 Å

- Motivate classical & quantum-mechanical descriptions of nuclei & electrons, respectively

Ehrenfest Molecular Dynamics (EMD)

- Small \hbar expansion, applied to the nucleus degrees-of-freedom, leads to mixed quantum (for electrons) & classical (for nuclei) dynamical equations

Classical Newton's equation of motion for nucleus positions

$$M_I \frac{d^2}{dt^2} \mathbf{R}_I = - \left\langle \Psi(t) \left| \frac{\partial h(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})}{\partial \mathbf{R}_I} \right| \Psi(t) \right\rangle$$
$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = h(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) |\Psi(t)\rangle$$

Time-dependent Schrödinger equation for the electronic wave function Ψ

- **See notes on:**
(1) QMD summary & (2) QMD equation

Derivation of EMD Equations (1)

- Dynamics of the electron-nucleus system is encoded in the scattering matrix (or S matrix) in the closed-time path integral form

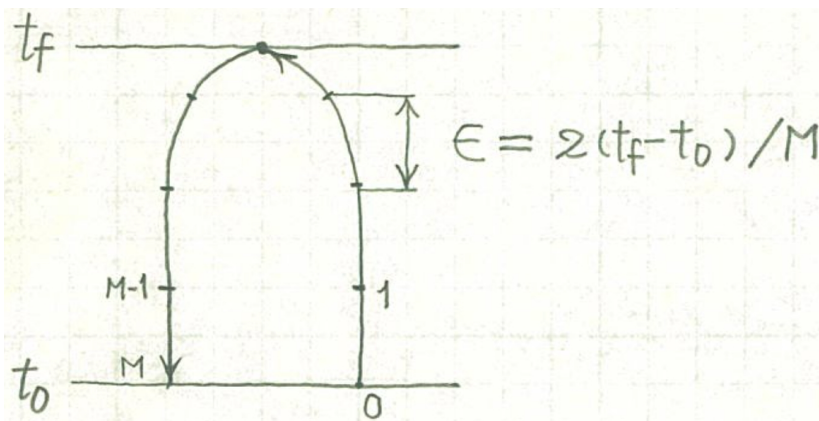
Unitary time propagator

$$S = \frac{1}{\sum_k \rho_k(\mathbf{R})} \sum_k \rho_k(\mathbf{R}) \langle k\mathbf{R} | U_-(t_0, t_f) U_+(t_f, t_0) | k\mathbf{R} \rangle$$

Initial probability of
(k, R) state at time t₀

k-th electronic state
with nucleus positions R

remote future



remote past

$$U_{\pm}(t, t') = T_{\pm} \exp \left(-\frac{i}{\hbar} \int_{t'}^t d\tau H_{\pm}(\tau) \right)$$

Time-ordering operator

- See notes on:

(1) unitary time propagation; (2) closed-time path integral; (3) QMD equation

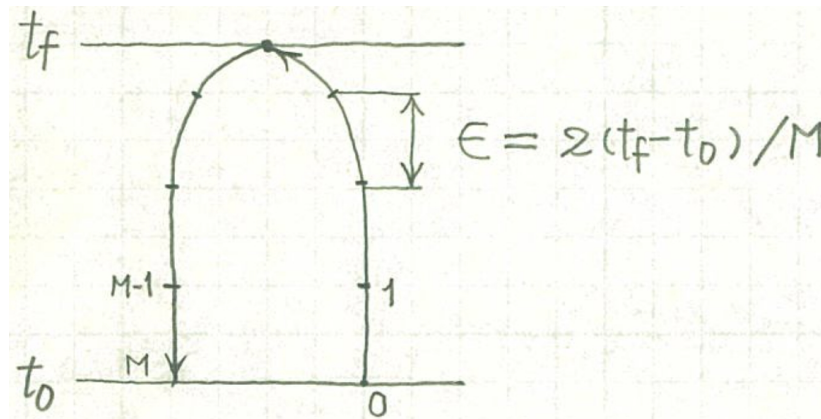
Derivation of EMD Equations (2)

- **Path-integral w.r.t. nucleus trajectories:** $H(t) = \frac{\mathbf{p}^2}{2M} + h(\mathbf{r}, \mathbf{R}, t)$

$$S = \int_{\text{path}, p}^{\mathbf{R}(t_0)=\mathbf{R}} D[\mathbf{R}(t)] \exp\left(\frac{i}{\hbar} S_0[\mathbf{R}(t)]\right) T[\mathbf{R}(t)]$$

$$S_0[\mathbf{R}(t)] = \int_p dt \frac{M}{2} \left(\frac{d\mathbf{R}}{dt}\right)^2$$

$$T[\mathbf{R}(t)] = \frac{1}{\sum_k \rho_k(\mathbf{R})} \sum_k \rho_k(\mathbf{R}) \langle k\mathbf{R} | T_p \exp\left[-\frac{i}{\hbar} \int_p dt h(\mathbf{r}, \mathbf{R}(t), t)\right] | k\mathbf{R} \rangle$$



- **See note on:**
QMD equation

Derivation of EMD Equations (3)

- Keep the leading term of the \hbar expansion (*i.e.* saddle-point approximation) of the path integral

$$\delta \left\{ S_0[\mathbf{R}(t)] + \frac{\hbar}{i} \ln T[\mathbf{R}(t)] \right\} = 0$$

which amounts to

$$M \frac{d^2}{dt^2} \mathbf{R}_I = - \frac{1}{\sum_k \rho_k(\mathbf{R})} \sum_k \rho_k(\mathbf{R}) \left\langle k(t) \mathbf{R} \left| \frac{\partial h(\mathbf{r}, \mathbf{R}(t), t)}{\partial \mathbf{R}(t)} \right| k(t) \mathbf{R} \right\rangle$$
$$i\hbar \frac{\partial}{\partial t} |k(t), \mathbf{R}\rangle = h(\mathbf{r}, \mathbf{R}(t), t) |k(t), \mathbf{R}\rangle$$

- See notes on
(1) QMD equation & (2) functional derivative

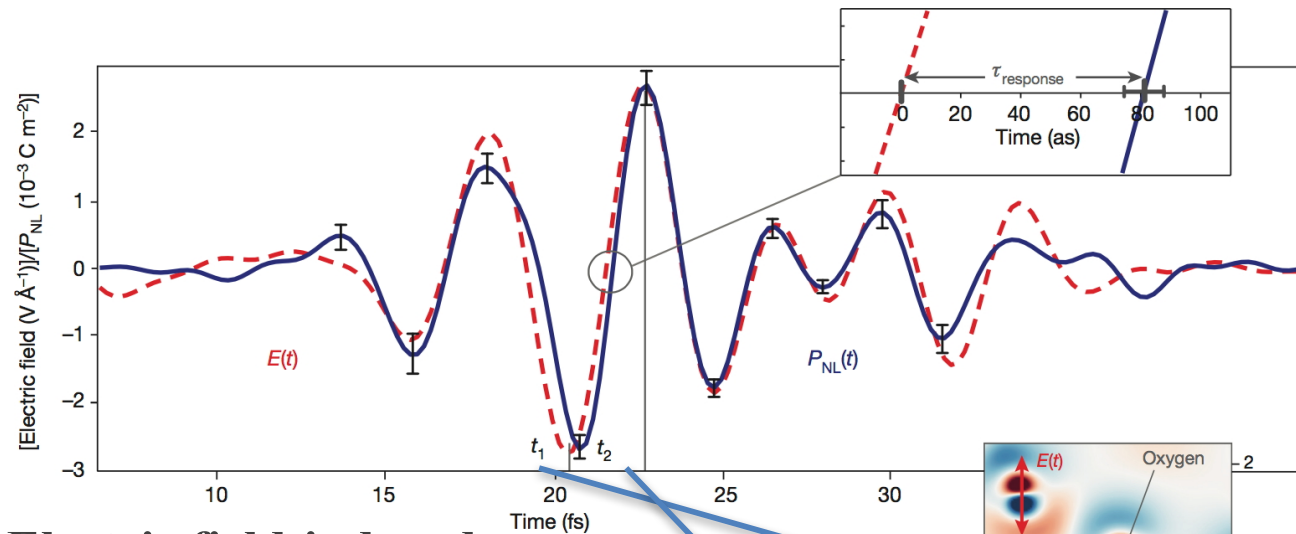
EMD Application: Electron Mobility

- **Electron transport in condensed matter under electric field \mathcal{E}**

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = h(\mathbf{r}, \{\mathbf{R}_I(t)\}, t)$$
$$h(\mathbf{r}, \{\mathbf{R}_I(t)\}, t) = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{\partial}{\partial \mathbf{r}} - e\mathcal{E}t \right)^2 + v(\mathbf{r}, \{\mathbf{R}_I(t)\})$$

- **For the computation of electronic conductivity & associated gauge transformation, see the note on** quantum dynamical computation of electronic conductivity
- A. Nakano, P. Vashishta & R. K. Kalia, “Electron transport in disordered systems: a nonequilibrium quantum molecular dynamics approach,” *Phys. Rev. B* **43**, 10928 ('91)
- A. Nakano, P. Vashishta & R. K. Kalia, “Probing localization & mobility of an excess electron in a-Si by quantum molecular dynamics,” *Phys. Rev. B* **45**, 8363 ('92)

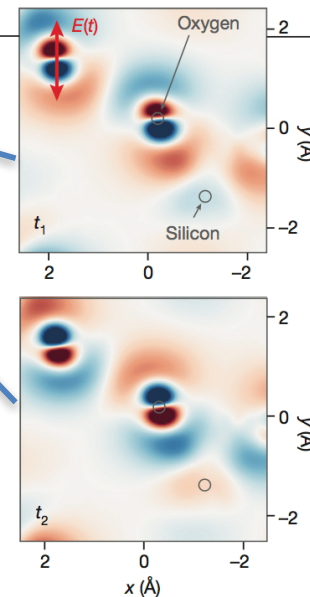
EMD Application: Attosecond Dynamics



**Electric field-induced
polarization in silica**

**Positive (red) & negative (blue)
change in charge density**

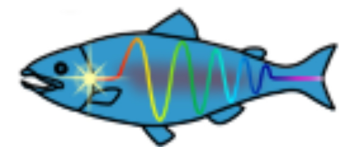
A. Sommer, K. Yabana *et al.*, "Attosecond nonlinear polarization & light-matter energy transfer in solids," *Nature* **534**, 86 ('16)



- **Ehrenfest dynamics codes by Prof. Kazuhiro Yabana's group**

ARTED: <https://github.com/ARTED/ARTED>

SALMON: <http://salmon-tddft.jp>



SALMON

Born-Oppenheimer Molecular Dynamics

- Due to the much larger nuclei masses (M_I) compared to the electron mass (m), the quantum-mechanical wave function of the system is separable to those of the electrons & nuclei
- At ambient conditions, the electronic wave function remains in its ground state ($|\Psi_0\rangle$) with the energy eigenvalue ϵ_0 , corresponding to the instantaneous nuclei positions ($\{\mathbf{R}_I\}$), with the latter following classical mechanics

$$M_I \frac{d^2}{dt^2} \mathbf{R}_I = - \frac{\partial}{\partial \mathbf{R}_I} \langle \Psi_0 | h(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) | \Psi_0 \rangle$$
$$h(\{\mathbf{r}_i\}, \{\mathbf{R}_I\}) | \Psi_0 \rangle = \epsilon_0 | \Psi_0 \rangle$$

- See notes on:
(1) QMD summary & (2) adiabatic approximation

Born-Oppenheimer (BO) MD Derivation (1)

- Expand the wave function in terms of the complete set of eigenstates, $\{\psi_k(\mathbf{r}, \mathbf{R})\}$, with fixed nuclei position \mathbf{R} (*i.e.*, adiabatic basis)

$$\psi(\mathbf{r}, \mathbf{R}, t) = \sum_k \chi_k(\mathbf{R}, t) \psi_k(\mathbf{r}, \mathbf{R})$$
$$h(\mathbf{r}, \mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R}) = E_k(\mathbf{R}) \psi_k(\mathbf{r}, \mathbf{R})$$

- Resulting time-dependent Schrödinger equation

$$\left[i\hbar \frac{\partial}{\partial t} + \sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} - E_k(\mathbf{R}) - T_{kk}(\mathbf{R}) \right] \chi_k(\mathbf{R}, t) = \sum_{k' \neq k} T_{kk'}(\mathbf{R}) \chi_{k'}(\mathbf{R}, t)$$
$$T_{kk'}(\mathbf{R}) = \sum_I \left\langle k \left| \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{R}_I} \right| k' \right\rangle \cdot \frac{\hbar}{iM_I} \frac{\partial}{\partial \mathbf{R}_I} - \sum_I \left\langle k \left| \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} \right| k' \right\rangle$$

Nonadiabatic coupling due to nuclei motion

- See notes on:
(1) QMD summary & (2) adiabatic approximation

Born-Oppenheimer (BO) MD Derivation (2)

- Born-Oppenheimer approximation neglects all T_{kk} terms; when in the electronic ground state ($k = 0$), off-diagonal transition is negligible if

$$|T_{k0}(\mathbf{R})| \ll E_k(\mathbf{R}) - E_0(\mathbf{R})$$

diagonal term T_{kk} was shown to be $O(m/M_I)$

- Classical limit of the resulting equation for nuclei can be derived using the same \hbar expansion as in the derivation of Ehrenfest MD

$$\left[i\hbar \frac{\partial}{\partial t} + \sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} - E_k(\mathbf{R}) \right] \chi_k(\mathbf{R}, t) = 0$$



$$M_I \frac{d^2}{dt^2} \mathbf{R}_I = - \frac{\partial}{\partial \mathbf{R}_I} E_k(\mathbf{R}) = - \left\langle k \left| \frac{\partial h(\mathbf{r}, \mathbf{R}, t)}{\partial \mathbf{R}} \right| k \right\rangle$$

Hellmann-Feynman theorem

- See notes on:

(1) QMD summary & (2) adiabatic approximation

Hellmann-Feynman Theorem

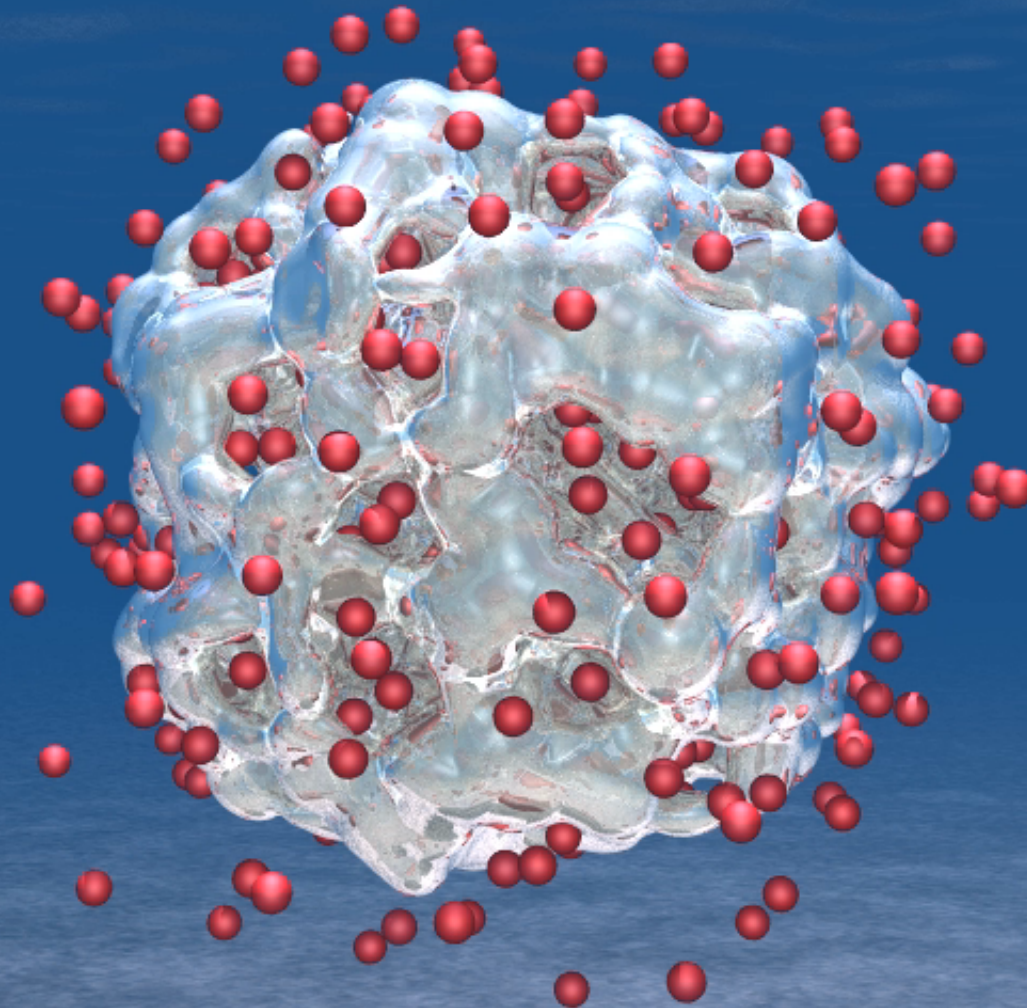
- Consider a Hamiltonian that include a parameter λ (in our case, nuclei positions \mathbf{R})

$$\begin{aligned}\frac{dE_\lambda}{d\lambda} &= \frac{d}{d\lambda} \langle \psi_\lambda | \hat{H}_\lambda | \psi_\lambda \rangle \\ &= \left\langle \frac{d\psi_\lambda}{d\lambda} | \hat{H}_\lambda | \psi_\lambda \right\rangle + \left\langle \psi_\lambda | \hat{H}_\lambda | \frac{d\psi_\lambda}{d\lambda} \right\rangle + \left\langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \right\rangle \\ &= E_\lambda \left\langle \frac{d\psi_\lambda}{d\lambda} | \psi_\lambda \right\rangle + E_\lambda \left\langle \psi_\lambda | \frac{d\psi_\lambda}{d\lambda} \right\rangle + \left\langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \right\rangle \\ &= E_\lambda \frac{d}{d\lambda} \langle \psi_\lambda | \psi_\lambda \rangle + \left\langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \right\rangle \\ &= \left\langle \psi_\lambda | \frac{d\hat{H}_\lambda}{d\lambda} | \psi_\lambda \right\rangle. \quad \langle \psi_\lambda | \psi_\lambda \rangle = 1\end{aligned}$$

BOMD Application: H₂ Production from Water

16,661-atom BOMD simulation of Li₄₄₁Al₄₄₁ in water on 786,432 IBM Blue Gene/Q cores

K. Shimamura *et al.*,
Nano Lett. **14**, 4090 ('14)



21,140 time steps (129,208 self-consistent-field iterations); unit time-step = 0.242 fs

Berry Phase

- The adiabatic basis (electronic eigenstates with fixed nucleus positions $\mathbf{R}(t)$ at each instance of time t) with energy $E_k(\mathbf{R})$, used here, plays a role in the discussion of Berry (or geometric) phase of electronic wave function during adiabatic turning-on/off of external potential

$$|k(t)\rangle = \exp(i\gamma_k(t)) \exp\left[-\frac{i}{\hbar} \int_0^t dt' E_k(\mathbf{R}(t'))\right] |k(t=0)\rangle$$

$$\gamma_k = \int_{\text{path}} d\mathbf{R} \cdot i \left\langle k(\mathbf{R}) \left| \frac{\partial}{\partial \mathbf{R}} \right| k(\mathbf{R}) \right\rangle$$

Berry phase

- Integration of the Berry phase along a closed path can be nonzero, which is observable (e.g. Aharonov-Bohm effect)
- QXMD uses it to compute electronic polarizability

Quantum-Mechanical Calculation of Polarization

- While polarization $\mathbf{P} = \int d\mathbf{r} \mathbf{r} |\psi(\mathbf{r})|^2$ is ill-defined under periodic boundary condition, its change $\Delta\mathbf{P} = \int_0^t dt' \mathbf{j}$ is well-defined, with a proper gauge to compute current \mathbf{j} (note on quantum dynamical computation of electronic conductivity)
- **Change of polarization upon adiabatic switching of finite electric field \mathcal{E} with periodic boundary condition**

R. Resta, *Phys. Rev. Lett.* **80**, 1800 ('98); P. Umari & A. Pasquarello, *ibid.* **89**, 157602 ('02)

$$\Delta P_{\text{el},x} = -\frac{L}{\pi} \text{Im}(\ln \det[\langle \psi_m | \exp(i2\pi x/L) | \psi_n \rangle]) \quad (m, n \in \{\text{occupied}\})$$
$$\{\psi_m\} = \text{argmin}(E_{\text{Kohn-Sham}}[\{\psi_m\}] - \mathcal{E} \Delta P_{\text{el},x}[\{\psi_m\}])$$

- **The above formula is equivalent to a sum of valence-band Berry phases**

R. D. King-Smith & D. Vanderbilt, *Phys. Rev. B* **47**, 1651('93); I. Souza, J. Iniguez & D. Vanderbilt, *Phys. Rev. Lett.* **89**, 117602 ('02)

$$\Delta \mathbf{P}_{\text{el}} = \int_0^{\mathcal{E}} d\lambda \frac{\partial \mathbf{P}_{\text{el}}}{\partial \lambda} = -\frac{ie}{(2\pi)^3} \sum_{n \in \{\text{occupied}\}} \int_{\text{Brillouin zone}} d\mathbf{k} \left\langle \psi_{n\mathbf{k}} \left| \frac{\partial}{\partial \mathbf{k}} \right| \psi_{n\mathbf{k}} \right\rangle$$

- **Above a critical field $\mathcal{E}_c \sim (\text{energy gap})/(\text{simulation cell size})$, the energy functional has no minimum, indicating Zener breakdown (*i.e.* tunneling from valence to conduction bands)**