Quantum Molecular Dynamics Basics

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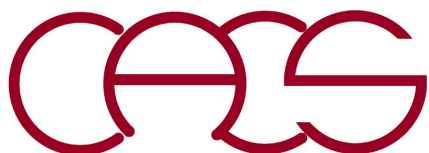*Collaboratory for Advanced Computing & Simulations*
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Objective

- **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**
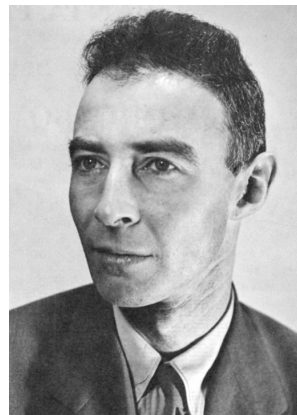   - **Electron & nucleus dynamics above femtosecond (10^{-15} s)**

     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, $\{\mathbf{r}_i | i = 1, \ldots, N\}$ & $\{\mathbf{R}_I | I = 1, \ldots, N_{\text{atom}}\}$**

$$H = \sum_{I=1}^{N_{\text{atom}}} \frac{\mathbf{P}_I^2}{2M_I} + h(\{\mathbf{r}_i\}, \{\mathbf{R}_I\})$$

$$= \sum_{I=1}^{N_{\text{atom}}} \left[\frac{\mathbf{P}_I^2}{2M_I} + V_{\text{ext}}(\mathbf{R}_I) \right] + \sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + v_{\text{ext}}(\mathbf{r}_i) \right]$$

$$+ \underbrace{\frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\substack{\text{electron-electron} \\ \text{interaction}}} - \underbrace{\sum_{i,J} \frac{Z_J e^2}{|\mathbf{r}_i - \mathbf{R}_J|}}_{\substack{\text{electron-nuclei} \\ \text{interaction}}} + \underbrace{\frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|}}_{\substack{\text{nuclei-nuclei} \\ \text{interaction}}}$$

- **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**

$$\Lambda_I = \frac{\hbar}{\sqrt{2\pi M_I k_{\mathrm{B}} T}} \ll \underset{\substack{\text{length scale} \\ \text{of interest in QMD}}}{\widetilde{\lambda}} \sim \Lambda_{\text{electron}} = \frac{\hbar}{\sqrt{2\pi m k_{\mathrm{B}} T}}$$

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**
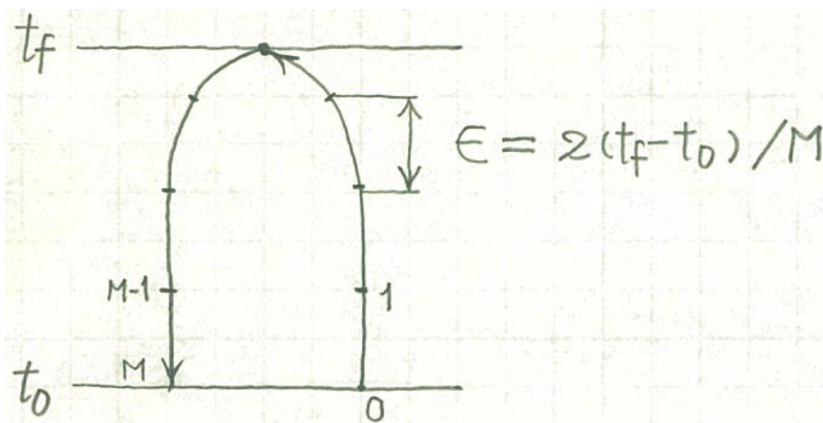
Unitary time propagator

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

Initial probability of $(k, \mathbf{R})$ state at time t_0

k-th electronic state with nucleus positions $\mathbf{R}$

remote future

$$\epsilon = 2(t_f - t_0)/M$$

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

Time-ordering operator

remote past

- **See notes on:**

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

K. Chou *et al.*, "Equilibrium & nonequilibrium formalisms made unified," *Phys. Rep.* **118**, 1 ('85)
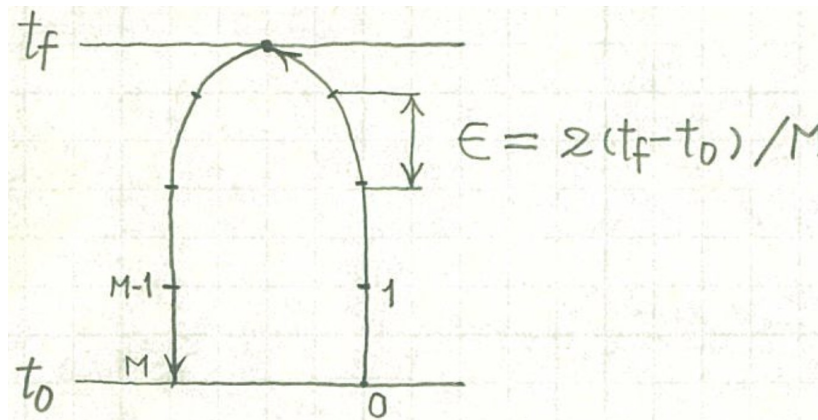
Derivation of EMD Equations (2)

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

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

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

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

$\epsilon = 2(t_f - t_0)/M$

- **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
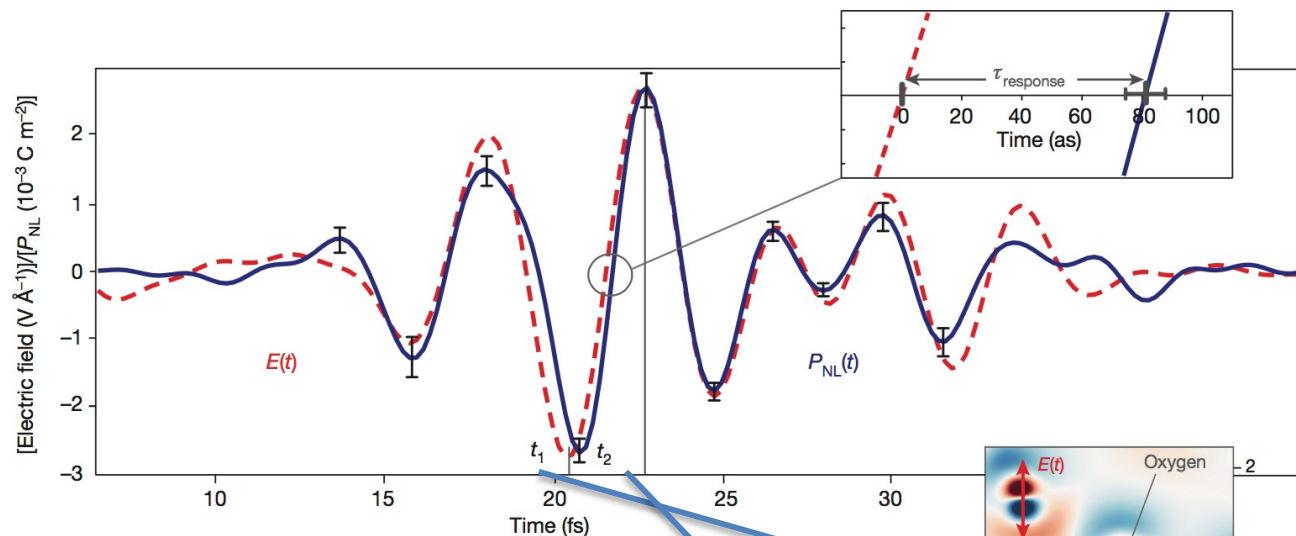
Electric field-induced polarization in silica

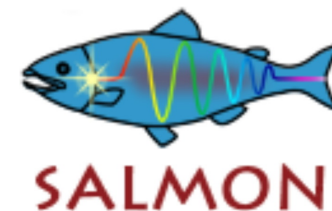**Positive (red) & negative (blue) change in charge density**
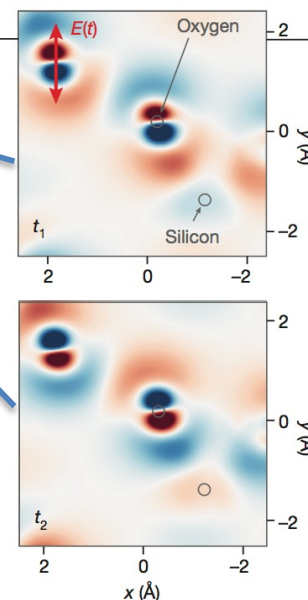
A. Sommer, K. Yabana *et al*., "Attosecond nonlinear polarization & light-matter energy transfer in solids," *Nature* **534**, 86 ('16)

- **Ehrenfest dynamics codes by Prof. Kazuhiro Yabana's group**
  ARTED: https://github.com/ARTED/ARTED
  SALMON: http://salmon-tddft.jp

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 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**

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

$$T_{kk'}(\mathbf{R}) = \sum_I \left\langle k\left|\frac{\hbar}{i}\frac{\partial}{\partial \mathbf{R}_I}\right|k'\right\rangle \bullet \frac{\hbar}{iM_I}\frac{\partial}{\partial \mathbf{R}_I} - \sum_I \left\langle k\left|\frac{\hbar^2}{2M_I}\frac{\partial^2}{\partial \mathbf{R}_I^2}\right|k'\right\rangle$$

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:**

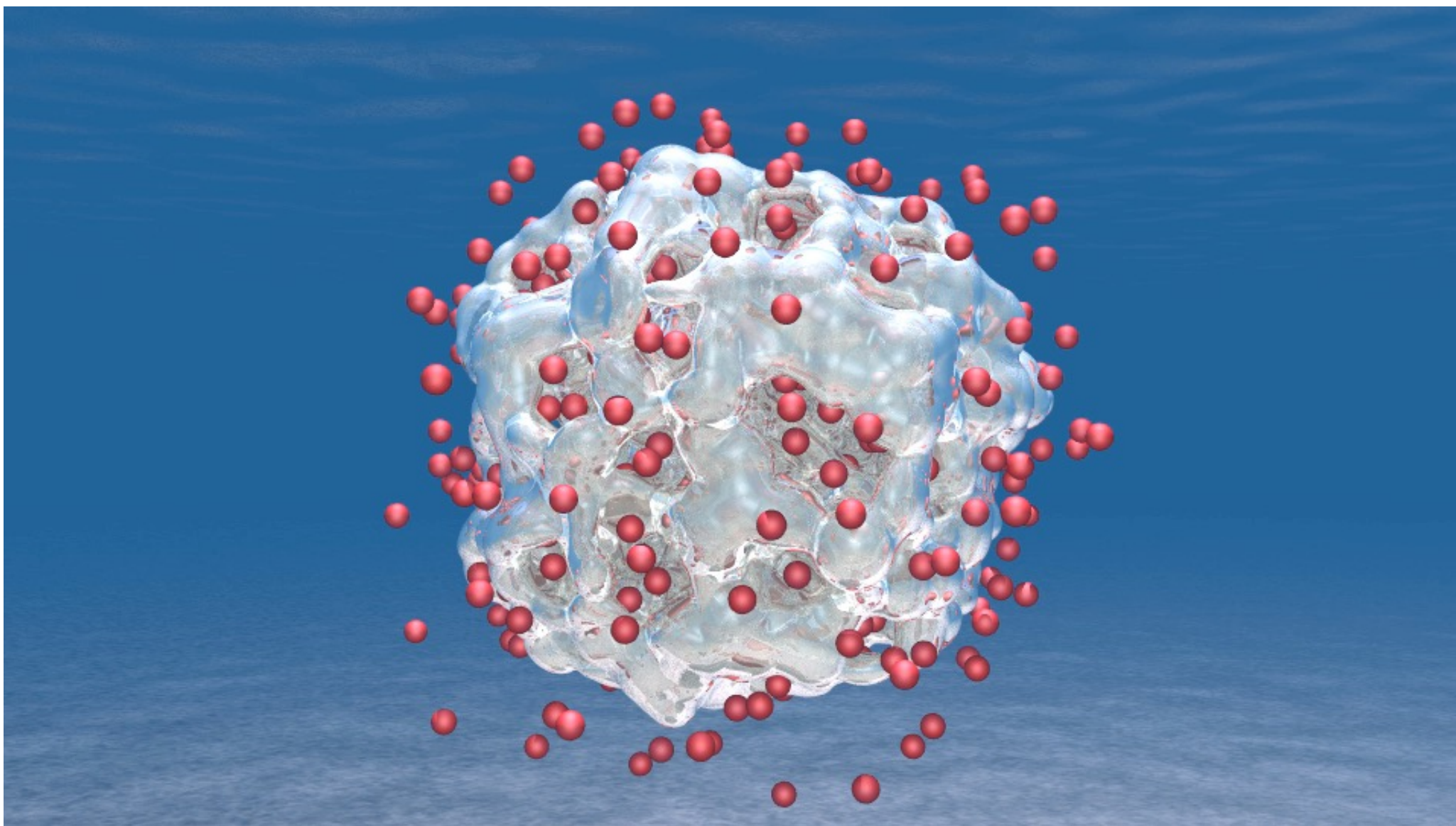(1) QMD summary & (2) adiabatic approximation

Hellmann-Feynman Theorem

- **Consider a Hamiltonian that include a parameter λ (in our case, nuclei positions R)**

$$\frac{\mathrm{d}E_\lambda}{\mathrm{d}\lambda} = \frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi_\lambda|\hat{H}_\lambda|\psi_\lambda\rangle$$

$$= \left\langle\frac{\mathrm{d}\psi_\lambda}{\mathrm{d}\lambda}\middle|\hat{H}_\lambda\middle|\psi_\lambda\right\rangle + \left\langle\psi_\lambda\middle|\hat{H}_\lambda\middle|\frac{\mathrm{d}\psi_\lambda}{\mathrm{d}\lambda}\right\rangle + \left\langle\psi_\lambda\middle|\frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda}\middle|\psi_\lambda\right\rangle$$

$$= E_\lambda\left\langle\frac{\mathrm{d}\psi_\lambda}{\mathrm{d}\lambda}\middle|\psi_\lambda\right\rangle + E_\lambda\left\langle\psi_\lambda\middle|\frac{\mathrm{d}\psi_\lambda}{\mathrm{d}\lambda}\right\rangle + \left\langle\psi_\lambda\middle|\frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda}\middle|\psi_\lambda\right\rangle$$

$$= E_\lambda\frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi_\lambda|\psi_\lambda\rangle + \left\langle\psi_\lambda\middle|\frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda}\middle|\psi_\lambda\right\rangle$$

$$= \left\langle\psi_\lambda\middle|\frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda}\middle|\psi_\lambda\right\rangle.$$

$$\langle\psi_\lambda|\psi_\lambda\rangle = 1$$

BOMD Application: H_2 Production from Water

16,661-atom BOMD simulation of $Li_{441}Al_{441}$ in water on 786,432 IBM Blue Gene/Q cores

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 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**

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

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

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**

D. Xiao *et al.*, "Berry phase effects on electronic properties," *Rev. Mod. Phys*. **82**, 1959 ('10)

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)

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

$$\{\psi_m\} = \text{argmin}\big(E_{\text{Kohn-Sham}}[\{\psi_m\}] - \mathcal{E}\Delta P_{\text{el},x}[\{\psi_m\}]\big)$$

- **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)

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

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