Quantum Molecular Dynamics Basics

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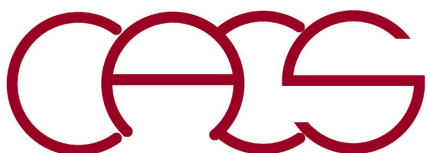*Collaboratory for Advanced Computing & Simulations*
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Objective

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

Time-dependent Schrödinger equation

1. **Ehrenfest molecular dynamics (EMD)**
   - **Solve 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)

   Electronic ground state

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

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

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

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

<p style="text-align:center;color:teal;">electron-electron interaction   electron-nuclei interaction   nuclei-nuclei interaction</p>

- **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**

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

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**
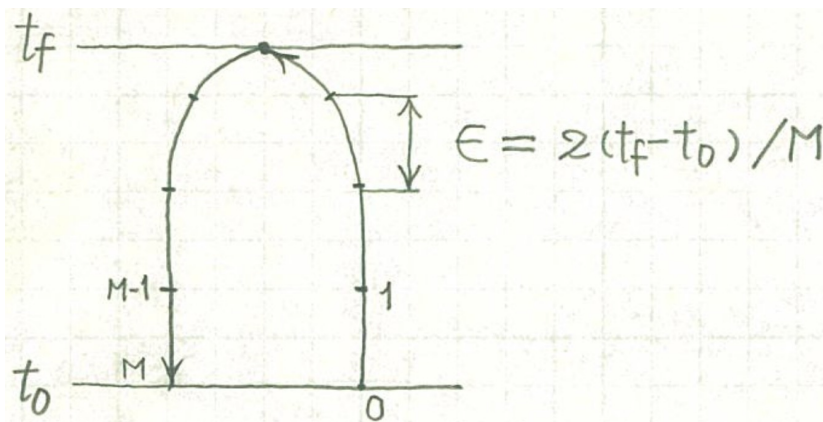
Unitary time propagator

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

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) <u>unitary time propagation</u>; (2) <u>closed-time path integral</u>; (3) <u>QMD equation</u>

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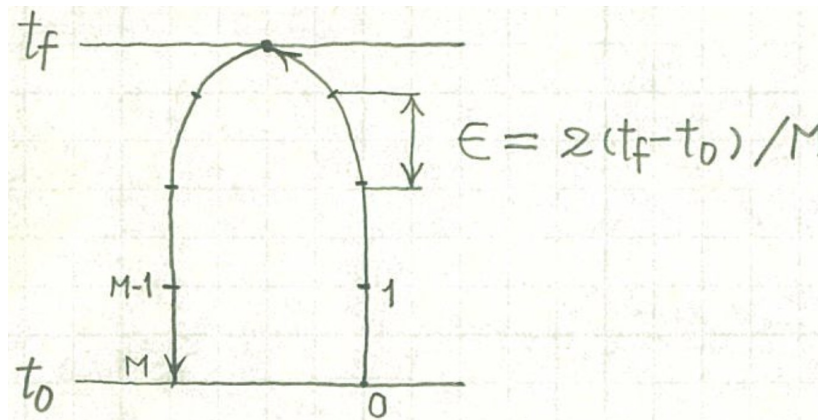
Derivation of EMD Equations (2)

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

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

Sum up all possible nuclei trajectories

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

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

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

- **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) functional derivative & (2) QMD equation

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
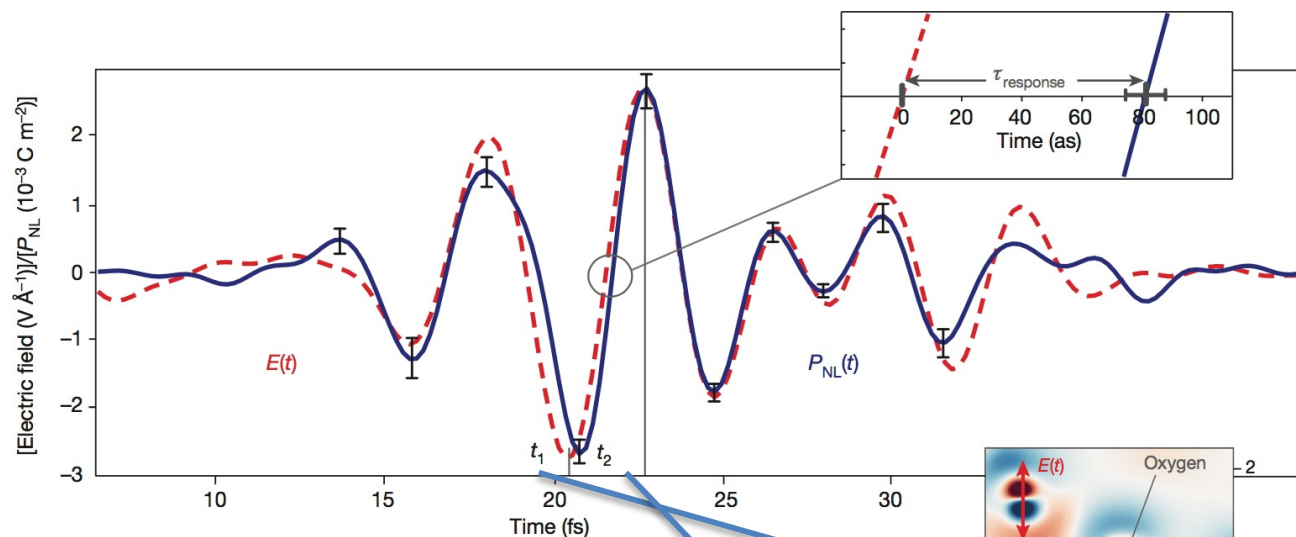
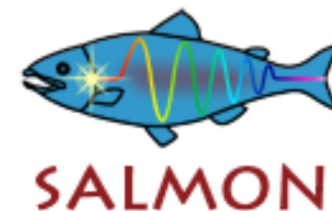**Electric field-induced polarization in silica**

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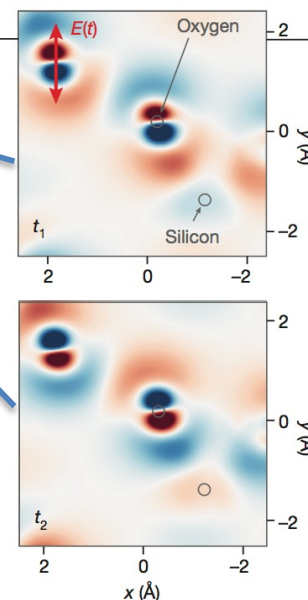
A. Sommer, K. Yabana *et al*., "Attosecond nonlinear polarization & light-matter energy transfer in solids," *Nature* **534**, 86 ('16)

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

  SALMON: http://salmon-tddft.jp

Dawn of Attosecond Physics

The Nobel Prize in Physics 2023

© Nobel Prize Outreach. Photo: Clément Morin
Pierre Agostini
Prize share: 1/3

© Nobel Prize Outreach. Photo: Clément Morin
Ferenc Krausz
Prize share: 1/3

© Nobel Prize Outreach. Photo: Clément Morin
Anne L'Huillier
Prize share: 1/3

The Nobel Prize in Physics 2023 was awarded to Pierre Agostini, Ferenc Krausz and Anne L'Huillier "for experimental methods that generate attosecond pulses of light for the study of electron dynamics in matter"

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 (*cf*. nonadiabatic QMD)

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

Nonadiabatic Quantum MD: DC-MESH

- **DC-MESH (divide-&-conquer Maxwell + Ehrenfest + surface-hopping):** $O(N)$ algorithm to simulate photo-induced quantum materials dynamics
- **LFD (local field dynamics):** Maxwell equations for light & real-time time-dependent density functional theory equations for electrons to describe light-matter interaction
- **QXMD (quantum molecular dynamics with excitation):** Nonadiabatic coupling of excited electrons & ionic motions based on surface-hopping approach
- **"Shadow" LFD (GPU)-QXMD (CPU) handshaking** *via* electronic occupation numbers with minimal CPU-GPU data transfer
- **GSLD:** Globally sparse (interdomain Hartree coupling *via* multigrid) & locally dense (intradomain nonlocal exchange-correlation computation *via* BLAS) solver
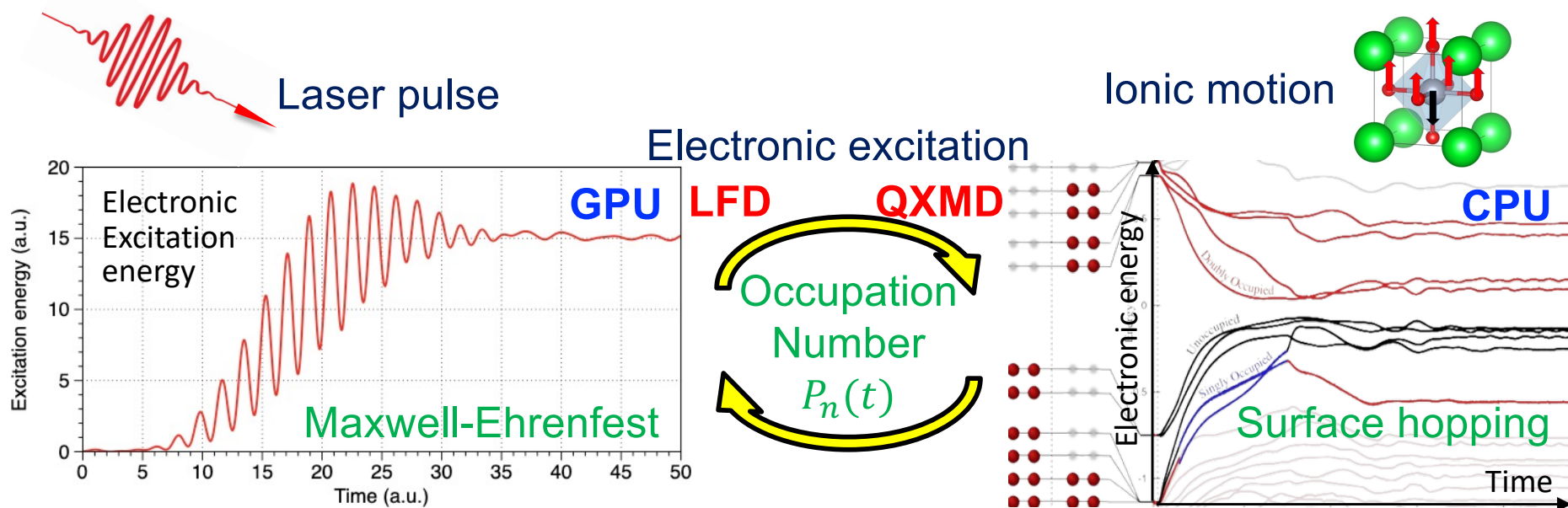
Linker *et al.*, *Science Adv*. **8**, eabk2625 (2022); Razakh *et al.*, *PDSEC* (IEEE, '24)

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)**

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

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

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

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

$$= \left\langle \psi_\lambda \middle| \frac{\mathrm{d}\hat{H}_\lambda}{\mathrm{d}\lambda} \middle| \psi_\lambda \right\rangle. \qquad \langle \psi_\lambda | \psi_\lambda \rangle = 1$$

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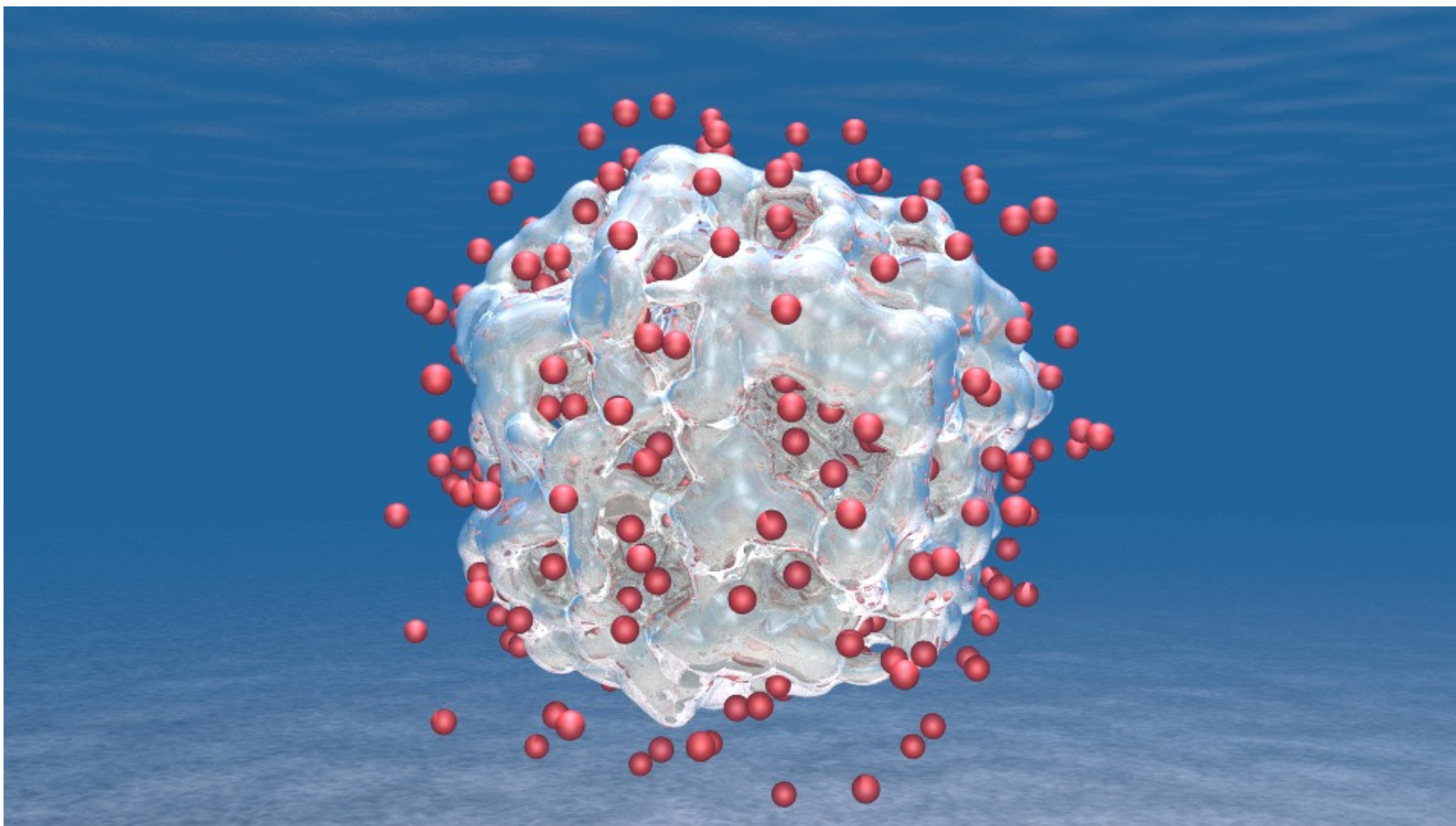
21,140 time steps (129,208 self-consistent-field iterations); unit time-step = 0.242 fs

Berry Phase

- **The adiabatic basis (electronic eigenstates with fixed nucleus positions R(t) at each instance of time t) with energy $E_k(R)$, 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)

D. Vanderbilt, *Berry Phases in Electronic Structure Theory* (Cambridge Univ. Press, '18)

Quantum-Mechanical Calculation of Polarization

- **While polarization $P = \int dr\, r|\psi(\mathbf{r})|^2$ is ill-defined under periodic boundary condition, its change $\Delta P = \int_0^t dt'\, \mathbf{j}$ 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)

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

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

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

Thickness dependence of dielectric constant of alumina films based on first-principles calculations

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ABSTRACT

Optoelectronic properties of devices made of two-dimensional materials depend largely on the dielectric constant and thickness of a substrate. To systematically investigate the thickness dependence of dielectric constant from first principles, we have implemented a double-cell method based on a theoretical framework by Martyna and Tuckerman [J. Chem. Phys. **110**, 2810 (1999)] and therewith developed a general and robust procedure to calculate dielectric constants of slab systems from electric displacement and electric field, which is free from material-specific adjustable parameters. We have applied the procedure to a prototypical substrate, Al_2O_3, thereby computing high-frequency and static dielectric constants of a finite slab as a function of the number of crystalline unit-cell layers. We find that two and four layers are sufficient for the high-frequency and static dielectric constants of (0001) Al_2O_3 slabs to recover 90% of the respective bulk values computed by a Berry-phase method. This method allows one to estimate the thickness dependence of dielectric constants for various materials used in emerging two-dimensional nanophotonics, while providing an analytic formula that can be incorporated into photonics simulations.