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Semiclassical Scaling in Quantum Dynamics:
"Who is epsilon?"

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Introduction: objective? “Semiclassical rescaling” of the nuclear time-dependent Schrödinger equation for a molecule within the Born-Oppenheimer approximation

Numerical analysis (maths)

- set epsilon (small parameter) and rescale variables
- assume semiclassical wavepacket ansatz
- determine error estimate wrt. epsilon power

Computational physics/chemistry

- set model Hamiltonian and initial condition/datum (mimic experiments)
- propagate approximate solution with numerical algorithm (integrator)
- check convergence of the solution (empirically)

Central problem: the error of an approximation

When can we pass to the semiclassical limit?

What are the conditions of validity?

What is the time when the approximation breaks enough?

→ Find out order of magnitude of error for given problem and final time (theory).

→ Determine final time for given problem within tolerance threshold on error (practice).

Point 1 (addressed here): who is epsilon in real life? (from system Hamiltonian / model)

Point 2 (to be further investigated): dependence on the initial condition? (dynamical regime)

Theoretical chemistry / molecular physics

$$i\hbar\frac{\partial}{\partial t}\psi^{\mathrm{v}}(Q,t)=\left(-\frac{\hbar^2}{2\mu}\Delta_Q+\frac{k}{2}Q^2\right)\psi^{\mathrm{v}}(Q,t).$$

Numerical / semiclassical analysis

$$i\varepsilon\frac{\partial}{\partial \tau}\psi^{\varepsilon}(Q,\tau)=\left(-\frac{\varepsilon^2}{2}\Delta_Q+\frac{k}{2}Q^2\right)\psi^{\varepsilon}(Q,\tau).$$

Formally looks as if only $\mu \rightsquigarrow 1$ and $\hbar \rightsquigarrow \varepsilon$, but not so simple…

→ Semiclassical regime: $\varepsilon \ll 1$ ($\approx 10^{-2}$) and $k\sim 1$ ($\delta Q\sim\sqrt{\varepsilon}$ and $\delta\tau=\varepsilon\delta t\sim 1$).

Natural atomic/electronic scaling

Hydrogen atom → define system of atomic units.

Galilean frame for the electron ~ centred at the proton ($m_\mathrm{e} \ll M_\mathrm{H}$).

Nonrelativistic electrostatic Hamiltonian in position representation

(position vector $\vec{r}_\mathrm{e}$, Laplacian operator $\Delta_{\vec{r}_\mathrm{e}}$, Euclidean norm $\|\vec{r}_\mathrm{e}\|$),

$$\hat{h}_\mathrm{e} = -\frac{\hbar^2}{2m_\mathrm{e}}\Delta_{\vec{r}_\mathrm{e}} - \frac{e^2}{4\pi\varepsilon_0\|\vec{r}_\mathrm{e}\|}.$$

Bound stationary states / discrete energies: eigensolutions, for $j \in \mathbb{N}^*$,

$$\hat{h}_\mathrm{e}\varphi_j^\mathrm{e}(\vec{r}_\mathrm{e}) = \epsilon_j^\mathrm{e}\varphi_j^\mathrm{e}(\vec{r}_\mathrm{e}).$$

One-particle Hilbert space $\mathcal{L}^2(\mathbb{R}^3 \to \mathbb{C})$ with orthonormal metric such that, for $j, k \in \mathbb{N}^*$,

$$\langle\varphi_j^\mathrm{e}|\varphi_k^\mathrm{e}\rangle = \iiint_{\{\mathbb{R}^3\}} \varphi_j^{\mathrm{e}*}(\vec{r}_\mathrm{e})\varphi_k^\mathrm{e}(\vec{r}_\mathrm{e})d\tau_\mathrm{e} = \delta_{jk}.$$

Physical constants / S.I. units (macroscopic values close to 1 on human scales, not for atoms):

- elementary charge $e = 1.60\ 10^{-19}$ C,
- electron mass $m_\mathrm{e} = 9.11\ 10^{-31}$ kg,
- dielectric permittivity of vacuum $\varepsilon_0 = 8.85\ 10^{-12}$ F m^{-1},
- reduced Planck constant (action quantum) $\hbar = \frac{h}{2\pi} = 1.05\ 10^{-34}$ J s → "stupidly" small…!

Get rid of them

→ better for numerical computations; easier for qualitative orders of magnitude.

First, rescale lengths in space wrt. a_0 ($\vec{r}_\mathrm{e} = a_0 \vec{r}'_\mathrm{e}$, $d\tau_\mathrm{e} = a_0^3 d\tau'_\mathrm{e}$) such that

$$\hat{h}_\mathrm{e} = -\frac{\hbar^2}{2m_\mathrm{e}a_0^2}\Delta_{\vec{r}'_\mathrm{e}} - \frac{e^2}{4\pi\varepsilon_0 a_0 \|\vec{r}'_\mathrm{e}\|},$$

$$\varphi'^\mathrm{e}_j(\vec{r}'_\mathrm{e}) = a_0^{3/2}\varphi^\mathrm{e}_j(\vec{r}_\mathrm{e}),$$

$$\left\langle \varphi^\mathrm{e}_j \middle| \varphi^\mathrm{e}_k \right\rangle = \iiint_{\{\mathbb{R}^3\}} \varphi'^{\mathrm{e}*}_j(\vec{r}'_\mathrm{e})\varphi'^\mathrm{e}_k(\vec{r}'_\mathrm{e}) d\tau'_\mathrm{e} = \delta_{jk}.$$

Now, rescale energies wrt. E_h from factors in kinetic and potential energy operators such that

$$\hat{h}_\mathrm{e} = -\frac{\hbar^2}{2m_\mathrm{e}a_0^2}\Delta_{\vec{r}_\mathrm{e}'} - \frac{e^2}{4\pi\varepsilon_0 a_0 \|\vec{r}_\mathrm{e}'\|},$$

$$\hat{h}_\mathrm{e} = E_\mathrm{h}\left(-\frac{1}{2}\Delta_{\vec{r}_\mathrm{e}'} - \frac{1}{\|\vec{r}_\mathrm{e}'\|}\right).$$

Hence,

$$\frac{\hbar^2}{m_\mathrm{e}a_0^2} = \frac{e^2}{4\pi\varepsilon_0 a_0} = E_\mathrm{h}.$$

Thus,

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_\mathrm{e}e^2},$$

$$E_\mathrm{h} = \frac{m_\mathrm{e}e^4}{(4\pi\varepsilon_0)^2\hbar^2}.$$

Ground-state energy,

$$\epsilon_1^{\mathrm{e}} = -\frac{E_{\mathrm{h}}}{2},$$

with ($1s$ orbital)

$$\varphi'^{\mathrm{e}}_1(\vec{r}'_{\mathrm{e}}) = \frac{1}{\sqrt{\pi}} e^{-\|\vec{r}'_{\mathrm{e}}\|},$$

i.e.,

$$\varphi_1^{\mathrm{e}}(\vec{r}_{\mathrm{e}}) = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-\frac{\|\vec{r}_{\mathrm{e}}\|}{a_0}}.$$

Excited-state energies, for $j \in \mathbb{N}^*$,

$$\epsilon_j^{\mathrm{e}} = -\frac{E_{\mathrm{h}}}{2j^2}.$$

→ natural length (a_0: bohr, atomic unit of length) and natural energy (E_{h}: Hartree, atomic unit of energy) scales: typical variations close to 1.

Virial theorem $\left[V\sim r^n \Longrightarrow \langle T\rangle = \frac{n}{2}\langle V\rangle; n=-1\right]$ (detailed here for the ground state):

$$r_\mathrm{e} = \|\vec{r}_\mathrm{e}\|,$$

$$\langle V\rangle_1 = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{\pi a_0^3}\int_0^\infty e^{-\frac{r_\mathrm{e}}{a_0}}\left(\frac{1}{r_\mathrm{e}}\right)e^{-\frac{r_\mathrm{e}}{a_0}}4\pi r_\mathrm{e}^2 dr_\mathrm{e} = -\frac{e^2}{\pi\varepsilon_0 a_0^3}a_0^2\underbrace{\int_0^\infty\left(\frac{r_\mathrm{e}}{a_0}\right)e^{-2\left(\frac{r_\mathrm{e}}{a_0}\right)}d\left(\frac{r_\mathrm{e}}{a_0}\right)}_{\frac{1}{4}} = -E_\mathrm{h},$$

$$\langle T\rangle_1 = -\frac{\hbar^2}{2m_\mathrm{e}}\frac{1}{\pi a_0^3}\int_0^\infty e^{-\frac{r_\mathrm{e}}{a_0}}\left(\frac{1}{r_\mathrm{e}^2}\frac{\partial}{\partial r_\mathrm{e}}r_\mathrm{e}^2\frac{\partial}{\partial r_\mathrm{e}}\right)e^{-\frac{r_\mathrm{e}}{a_0}}4\pi r_\mathrm{e}^2 dr_\mathrm{e}$$

$$= \underbrace{\frac{4\hbar^2}{m_\mathrm{e}a_0^4}a_0^2\underbrace{\int_0^\infty\left(\frac{r_\mathrm{e}}{a_0}\right)e^{-2\left(\frac{r_\mathrm{e}}{a_0}\right)}d\left(\frac{r_\mathrm{e}}{a_0}\right)}_{\frac{1!}{2^2}=\frac{1}{4}}}_{E_\mathrm{h}} \underbrace{-\frac{2\hbar^2}{m_\mathrm{e}a_0^5}a_0^3\underbrace{\int_0^\infty\left(\frac{r_\mathrm{e}}{a_0}\right)^2 e^{-2\left(\frac{r_\mathrm{e}}{a_0}\right)}d\left(\frac{r_\mathrm{e}}{a_0}\right)}_{\frac{2!}{2^3}=\frac{1}{4}}}_{E_\mathrm{h}/2} = \frac{E_\mathrm{h}}{2},$$

$$\epsilon_1^\mathrm{e} = \langle H\rangle_1 = \langle T\rangle_1 + \langle V\rangle_1 = \frac{E_\mathrm{h}}{2} - E_\mathrm{h} = -\frac{E_\mathrm{h}}{2}.$$

Now, introduce atomic unit of time (consistent with Heisenberg/Fourier relationships),

$$\tau_{\mathrm{e}} = \frac{\hbar}{E_{\mathrm{h}}} = \frac{(4\pi\varepsilon_0)^2\hbar^3}{m_{\mathrm{e}}e^4}.$$

S.I. values are $E_{\mathrm{h}} = 4.36\ 10^{-18}$ J, $a_0 = 5.29\ 10^{-11}$ m, and $\tau_{\mathrm{e}} = 2.42\ 10^{-17}$ s.

→ System of atomic units (mechanical: [M], [L], [T]),

$$a_0 = 1\ [\mathrm{L}],$$

$$E_{\mathrm{h}} = 1\ [\mathrm{ML^2T^{-2}}],$$

$$\tau_{\mathrm{e}} = 1\ [\mathrm{T}],$$

with

$$e^2/4\pi\varepsilon_0 = 1\ [\mathrm{ML^3T^{-2}}],$$

$$\hbar = 1\ [\mathrm{ML^2T^{-1}}],$$

$$m_{\mathrm{e}} = 1\ [\mathrm{M}].$$

N.B.: electrical [I] hidden in ratio $e^2/4\pi\varepsilon_0$, but add $e = 1\ [\mathrm{TI}]$ and $4\pi\varepsilon_0 = 1\ [\mathrm{M^{-1}L^{-3}T^4I^2}]$.

Effect of time rescaling? Getting rid of $\hbar$ and E_h in the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\psi'^{\mathrm{e}}(\vec{r}_\mathrm{e}',t)=E_\mathrm{h}\left(-\frac{1}{2}\Delta_{\vec{r}_\mathrm{e}'}-\frac{1}{\|\vec{r}_\mathrm{e}'\|}\right)\psi'^{\mathrm{e}}(\vec{r}_\mathrm{e}',t).$$

Setting

$$t=\tau_\mathrm{e}t'=\frac{\hbar}{E_\mathrm{h}}t',\qquad \frac{\partial}{\partial t}=\frac{1}{\tau_\mathrm{e}}\frac{\partial}{\partial t'}=\frac{E_\mathrm{h}}{\hbar}\frac{\partial}{\partial t'}\qquad\text{and}\qquad \psi'^{\mathrm{e}}(\vec{r}_\mathrm{e}',t)=\psi''^{\mathrm{e}}(\vec{r}_\mathrm{e}',t'),$$

yields

$$i\frac{\partial}{\partial t'}\psi''^{\mathrm{e}}(\vec{r}_\mathrm{e}',t')=\left(-\frac{1}{2}\Delta_{\vec{r}_\mathrm{e}'}-\frac{1}{\|\vec{r}_\mathrm{e}'\|}\right)\psi''^{\mathrm{e}}(\vec{r}_\mathrm{e}',t').$$

→ Physical constants are all removed: dimensionless differential equation wrt. energy variation, length in space, and duration in time.

→ Every significant variation is close to 1 within the system of atomic units.

Natural vibrational/nuclear scaling

Quantum linear harmonic oscillator (*e.g.*, vibration of H_2 molecule).

Normal coordinate, Q, reduced mass, μ, force constant, k.

Vibrational Hamiltonian in position representation,

$$\hat{h}_{\mathrm{v}} = -\frac{\hbar^2}{2\mu}\Delta_Q + \frac{k}{2}Q^2.$$

Ground-state eigensolution,

$$\omega = \sqrt{\frac{k}{\mu}},$$

$$\varphi_0^{\mathrm{v}}(Q) = \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\mu\omega Q^2}{2\hbar}\right),$$

$$\epsilon_0^{\mathrm{v}} = \frac{\hbar\omega}{2}.$$

Bound stationary states / discrete energies: eigensolutions, for $j \in \mathbb{N}$,

$$\hat{h}_{\mathrm{v}} \varphi_j^{\mathrm{v}}(Q) = \epsilon_j^{\mathrm{v}} \varphi_j^{\mathrm{v}}(Q).$$

One-particle Hilbert space $\mathcal{L}^2(\mathbb{R} \to \mathbb{C})$ with orthonormal metric such that, for $j, k \in \mathbb{N}$,

$$\left\langle \varphi_j^{\mathrm{v}} \middle| \varphi_k^{\mathrm{v}} \right\rangle = \int_{\{\mathbb{R}\}} \varphi_j^{\mathrm{v}*}(Q) \varphi_k^{\mathrm{v}}(Q) dQ = \delta_{jk}.$$

Excited-state energies, for $j \in \mathbb{N}$,

$$\epsilon_j^{\mathrm{v}} = \hbar\omega \left(j + \frac{1}{2} \right).$$

Ground-state probability density: square-modulus of $\varphi_0^{\mathrm{v}}(Q)$,

$$\rho_0^{\mathrm{v}}(Q) = |\varphi_0^{\mathrm{v}}(Q)|^2 = \sqrt{\frac{\mu\omega}{\pi\hbar}} \exp\left(-\frac{\mu\omega Q^2}{\hbar} \right) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{Q}{\sigma}\right)^2}.$$

→ Normal distribution with a zero mean (centred at $Q = \langle Q \rangle_0 = 0$) and a standard deviation (width) $\sigma = \sqrt{\langle Q^2 \rangle_0 - \langle Q \rangle_0^2} = \sqrt{\frac{\hbar}{2\mu\omega}}$.

First usual rescaling: mass weighting (isoinertial normal coordinates in many dimensions)

Mass-weighted coordinates, $q = \sqrt{\mu}Q$, such that

$$\hat{h}_{\mathrm{v}} = -\frac{\hbar^2}{2}\Delta_q + \frac{\omega^2}{2}q^2.$$

Many dimensions: unitary diagonalisation of the matrix generalisation of $\omega^2 = k/\mu$

→ normal modes.

Ground-state wavefunction, now normalised using $dq = \sqrt{\mu}dQ$, *i.e.*,

$$\varphi'^{\mathrm{v}}_0(q) = \mu^{-1/4}\varphi^{\mathrm{v}}_0(Q) = \left(\frac{\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\omega q^2}{2\hbar}\right).$$

Standard deviation (width),

$$\sigma' = \sqrt{\frac{\hbar}{2\omega}}.$$

Second usual rescaling: adimensionalisation (so-called frequency-mass-weighted normal coordinates)

Introduce natural length unit,

$$\beta = \sqrt{\frac{\hbar}{\mu\omega}},$$

such that, for $\mathcal{Q} = Q/\beta$,

$$\hat{h}_{\mathrm{v}} = \hbar\omega\left(-\frac{1}{2}\Delta_{\mathcal{Q}} + \frac{1}{2}\mathcal{Q}^2\right).$$

Natural unit of energy: $\hbar\omega$.

Ground-state wavefunction, normalised using $d\mathcal{Q} = \frac{1}{\beta}dQ$,

$$\varphi''^{\mathrm{v}}_0(\mathcal{Q}) = \sqrt{\beta}\varphi^{\mathrm{v}}_0(Q) = \frac{1}{\pi^{1/4}}e^{-\frac{Q^2}{2}}.$$

Standard deviation (width): $\sigma'' = \frac{1}{\sqrt{2}}$, *i.e.*, $\sigma = \beta\sigma'' = \frac{\beta}{\sqrt{2}}$.

Effect of time rescaling? Getting rid of $\hbar$ and $\hbar\omega$ in the time-dependent Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\psi''^{\mathrm{v}}(Q,t) = \hbar\omega\left(-\frac{1}{2}\Delta_Q + \frac{1}{2}Q^2\right)\psi''^{\mathrm{v}}(Q,t).$$

Setting

$$t = \tau_{\mathrm{v}}t' = \frac{\hbar}{\hbar\omega}t', \qquad \frac{\partial}{\partial t} = \frac{1}{\tau_{\mathrm{v}}}\frac{\partial}{\partial t'} = \frac{\hbar\omega}{\hbar}\frac{\partial}{\partial t'} \quad \text{and} \quad \psi''^{\mathrm{v}}(Q,t) = \psi'''^{\mathrm{v}}(Q,t'),$$

yields

$$i\frac{d}{dt'}\psi'''^{\mathrm{v}}(Q,t') = \left(-\frac{1}{2}\Delta_Q + \frac{1}{2}Q^2\right)\psi'''^{\mathrm{v}}(Q,t').$$

Alternatively: use period, $T = \frac{2\pi}{\omega}$ ($\tau_{\mathrm{v}} = \frac{\hbar}{\hbar\omega} = \frac{T}{2\pi}$), $t = Tt'$, and $\psi''^{\mathrm{v}}(Q,t) = \psi'''^{\mathrm{v}}(Q,t')$, yields

$$i\frac{d}{dt'}\psi'''^{\mathrm{v}}(Q,t') = 2\pi\left(-\frac{1}{2}\Delta_Q + \frac{1}{2}Q^2\right)\psi'''^{\mathrm{v}}(Q,t').$$

→ Physical constants are all removed: dimensionless differential equation wrt. energy variation, length in space, and duration in time.

Virial theorem $\left[V\sim Q^n \Longrightarrow \langle T\rangle = \frac{n}{2}\langle V\rangle; n=2\right]$ (detailed here for the ground state):

$$\langle V\rangle_0 = \frac{\mu\omega^2}{2}\left(\frac{\mu\omega}{\pi\hbar}\right)^{1/2}\int_{-\infty}^{+\infty} e^{-\frac{\mu\omega Q^2}{2\hbar}}(Q^2)e^{-\frac{\mu\omega Q^2}{2\hbar}}dQ = \frac{\mu\omega^2}{2}\left(\frac{\mu\omega}{\pi\hbar}\right)^{1/2}\underbrace{\int_{-\infty}^{+\infty}(Q^2)e^{-\frac{\mu\omega Q^2}{\hbar}}dQ}_{\frac{1}{2}\sqrt{\pi\left(\frac{\hbar}{\mu\omega}\right)^3}} = \frac{\hbar\omega}{4},$$

$$\langle T\rangle_0 = -\frac{\hbar^2}{2\mu}\left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{1}{2}}\int_{-\infty}^{+\infty} e^{-\frac{\mu\omega Q^2}{2\hbar}}\left(\frac{\partial^2}{\partial Q^2}\right)e^{-\frac{\mu\omega Q^2}{2\hbar}}dQ$$

$$= \frac{\hbar^2}{2\mu}\left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{1}{2}}\frac{\mu\omega}{\hbar}\underbrace{\int_{-\infty}^{+\infty} e^{-\frac{\mu\omega Q^2}{\hbar}}dQ}_{\sqrt{\pi\frac{\hbar}{\mu\omega}}} - \frac{\hbar^2}{2\mu}\left(\frac{\mu\omega}{\pi\hbar}\right)^{\frac{1}{2}}4\left(\frac{\mu\omega}{2\hbar}\right)^2\underbrace{\int_{-\infty}^{+\infty}(Q^2)e^{-\frac{\mu\omega Q^2}{\hbar}}dQ}_{\frac{1}{2}\sqrt{\pi\left(\frac{\hbar}{\mu\omega}\right)^3}} = \frac{\hbar\omega}{4},$$

$$\epsilon_0^{\mathrm{v}} = \langle H\rangle_0 = \langle T\rangle_0 + \langle V\rangle_0 = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} = \frac{\hbar\omega}{2}.$$

H_2 protype: orders of magnitude for energy, length, and time

Reduced atomic mass: $\mu = \frac{M_\mathrm{H}}{2} = 918.6\ m_\mathrm{e}$.

(usual approximation: atomic mass rather than bare nuclear mass, 918.1 m_e).

Experimentally, $\bar{\sigma} = 4401$ cm^{-1}: $\hbar\omega = 0.02005\ E_\mathrm{h}$.

Corresponding oscillation period $T = 2\pi\tau_\mathrm{v} = 313.3\ \tau_\mathrm{e}$.

Natural length: $\beta = 0.2330\ a_0$.

Organic molecules

Reduced masses $\mu \sim$ 2000 to 20000 m_e.

Vibrational modes with $\bar{\sigma} \sim$ 300 to 3000 cm^{-1} ($\hbar\omega \sim$ 0.0015 to 0.015 E_h).

Electronic transition energies, UV-visible, $\sim$ 0.05 to 0.5 E_h (1.4 $\sim$ 14 eV).

Representative ratio of time scales $\sim$ 10^{-2} → semiclassical epsilon

Semiclassical scaling

Back to

$$i\hbar \frac{d}{dt}\psi^{\mathrm{v}}(Q,t) = \hat{h}_{\mathrm{v}}\psi^{\mathrm{v}}(Q,t),$$

where

$$\hat{h}_{\mathrm{v}} = -\frac{\hbar^2}{2\mu}\Delta_Q + \frac{k}{2}Q^2.$$

Rescale to atomic units:

$$\frac{\mu}{m_{\mathrm{e}}}, \qquad \frac{Q}{a_0}, \qquad \frac{t}{\tau_{\mathrm{e}}}, \qquad \frac{\hat{h}_{\mathrm{v}}}{E_{\mathrm{h}}}, \qquad \frac{\hbar}{\hbar}, \qquad \frac{k}{E_{\mathrm{h}}a_0^{-2}}.$$

→ **Small parameter:**

$$\varepsilon = \sqrt{\frac{m_{\mathrm{e}}}{\mu}} \approx 10^{-2}.$$

Using implicit atomic units yields

$$i\frac{d}{dt}\psi^{\mathrm{v}}(Q,t) = \left(-\frac{\varepsilon^2}{2}\Delta_Q + \frac{k}{2}Q^2\right)\psi^{\mathrm{v}}(Q,t).$$

Rescaling time,

$$\tau = \varepsilon t,$$

further yields

$$i\varepsilon\frac{d}{d\tau}\tilde{\psi}^{\mathrm{v}}(Q,\tau) = \left(-\frac{\varepsilon^2}{2}\Delta_Q + \frac{k}{2}Q^2\right)\tilde{\psi}^{\mathrm{v}}(Q,\tau).$$

where $\tilde{\psi}^{\mathrm{v}}(Q,\tau) = \psi^{\mathrm{v}}(Q,t)$.

→ **Semiclassical formulation.**

Powers of epsilon within the Born-Oppenheimer approximation

System-dependent parameters: reduced mass μ and force constant k

→ $\frac{\mu}{m_\mathrm{e}}$ determines the definition of ε:

$$\mu = \varepsilon^{-2} m_\mathrm{e} = \varepsilon^{-2} \text{ a.u.}$$

→ $\frac{\sqrt{k}}{E_\mathrm{h}^{1/2} a_0^{-1}}$ is usually close to 1 (see later on)

Harmonic oscillator:

$$\omega = \sqrt{\frac{k}{\mu}}, \qquad \Delta E_\mathrm{v} = \hbar\omega = \varepsilon\hbar\sqrt{\frac{k}{m_\mathrm{e}}} \approx \varepsilon \frac{\hbar}{a_0}\sqrt{\frac{E_\mathrm{h}}{m_\mathrm{e}}} = \varepsilon \frac{\hbar^2}{m_\mathrm{e} a_0^2} = \varepsilon E_\mathrm{h}.$$

owing to $E_\mathrm{h} = \frac{\hbar^2}{m_\mathrm{e} a_0^2} = \frac{e^2}{4\pi\varepsilon_0 a_0}$.

$$\Delta E_\mathrm{v} \approx \varepsilon E_\mathrm{h} = \varepsilon \text{ a.u.} \quad \text{and} \quad \tau_\mathrm{v} = \frac{\hbar}{E_\mathrm{v}} \approx \varepsilon^{-1}\tau_\mathrm{e} = \varepsilon^{-1} \text{ a.u.}$$

Example 1: H_2 (1 mode / GS)

$$\mu = 900\, m_{\mathrm{e}}$$

$$\varepsilon = 0.03$$

$$\sqrt{k} = 0.6\, E_{\mathrm{h}}^{1/2} a_0^{-1}$$

$$\Delta E_{\mathrm{v}} = 0.02\, E_{\mathrm{h}}$$

$$\tau_{\mathrm{v}} = 50\, \tau_{\mathrm{e}}$$

Example 2: pyrazine (24 modes / GS)

μ ranges from 2000 to 16000 a.u. (ave. 6000)

ε from 0.008 to 0.02 (ave. 0.02)

$\sqrt{k}$ from 0.1 to 0.9 a.u. (ave. 0.4)

ΔE_{v} from about 0.002 to 0.01 a.u. (ave. 0.006)

Length scale?

$$\hat{h}_{\mathrm{v}} = -\frac{\hbar^2}{2\mu}\Delta_Q + \frac{k}{2}Q^2,$$

$$\varphi_0^{\mathrm{v}}(Q) = \frac{1}{\pi^{1/4}}\frac{1}{\sqrt{\beta}}e^{-\frac{1}{2}\left(\frac{Q}{\beta}\right)^2},$$

$$\beta = \sqrt{\frac{\hbar}{\mu\omega}} = \varepsilon\sqrt{\frac{\hbar}{m_{\mathrm{e}}\omega}} \approx \varepsilon\sqrt{\frac{\hbar^2}{m_{\mathrm{e}}\varepsilon E_{\mathrm{h}}}} = \sqrt{\varepsilon}a_0,$$

$$\delta Q = \beta \approx \sqrt{\varepsilon}a_0 = \sqrt{\varepsilon}\ \text{a.u.}$$

H_2 example: $\varepsilon = 0.03$ and $\beta = 0.2$ a.u.

Pyrazine example: ε ranges from 0.008 to 0.02 (ave. 0.02), β from 0.1 to 0.4 (ave. 0.2) a.u.

Momentum scale?

Unitary Fourier transform,

$$\tilde{\varphi}_0^{\mathrm{v}}\left(\frac{P}{\hbar}\right) = \frac{1}{\pi^{1/4}}\sqrt{\beta}\, e^{-\frac{1}{2}\left(\beta\frac{P}{\hbar}\right)^2}.$$

Natural momentum size,

$$\frac{\hbar}{\beta} = \sqrt{\hbar\mu\omega}.$$

$$\delta P = \frac{\hbar}{\beta} \approx \frac{1}{\sqrt{\varepsilon}}\hbar a_0^{-1} = \frac{1}{\sqrt{\varepsilon}}\ \text{a.u.}$$

N.B.: Heisenberg uncertainty “limit” in terms of standard deviations,

$$\sigma = \frac{\beta}{\sqrt{2}}, \qquad \tilde{\sigma} = \frac{\hbar}{\sqrt{2}\beta}, \qquad \sigma\tilde{\sigma} = \frac{\hbar}{2}.$$

Rescaled time, momentum, and action

Assuming atomic units and rescaling,

$$t \to \tau = \varepsilon t,$$

$$P \to p = \varepsilon P,$$

$$S \to s = \varepsilon S.$$

→ Same effect as $\hbar \to \varepsilon$ ("grain" of phase space):

$$i\hbar \frac{\partial}{\partial t} \to i\varepsilon \frac{\partial}{\partial \tau},$$

$$\hat{P} = \frac{\hbar}{i}\frac{\partial}{\partial Q} \to \hat{p} = \frac{\varepsilon}{i}\frac{\partial}{\partial Q},$$

$$e^{i\frac{S(t)}{\hbar}} \to e^{i\frac{s(\tau)}{\varepsilon}}.$$

Summary

Semiclassical wavepacket ansatz:

$$\tilde{\psi}^{\mathrm{v}}(Q,\tau) = \frac{1}{\varepsilon^{1/4}} u\left(\frac{Q-\langle Q_\tau\rangle}{\sqrt{\varepsilon}},\tau\right) e^{i\frac{\langle p_\tau\rangle(Q-\langle Q_\tau\rangle)}{\varepsilon}} e^{i\frac{s(\tau)}{\varepsilon}},$$

$$i\varepsilon\frac{d}{d\tau}\tilde{\psi}^{\mathrm{v}}(Q,\tau) = \left(-\frac{\varepsilon^2}{2}\Delta_Q + \frac{k}{2}Q^2\right)\tilde{\psi}^{\mathrm{v}}(Q,\tau).$$

$$Q\sim\sqrt{\varepsilon}, \qquad E\sim\varepsilon,$$

$$t\sim\frac{1}{\varepsilon}\rightarrow\tau\sim 1,$$

$$P\sim\frac{1}{\sqrt{\varepsilon}}\rightarrow p\sim\sqrt{\varepsilon},$$

$$PQ\sim 1\rightarrow pQ\sim\varepsilon,$$

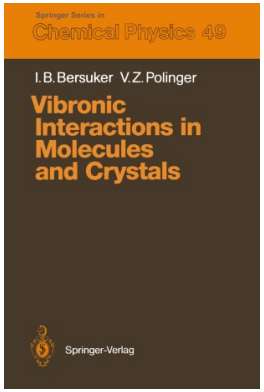
$$S\sim 1\rightarrow s\sim\varepsilon.$$

Controversy?

The scales above are consistent with Bersuker and Polinger ’89, p. 9 [DOI: 10.1007/978-3-642-83479-0] when they justify

$$k \sim \frac{e^2}{4\pi\varepsilon_0}\frac{1}{a_0^3} = 1 \text{ u.a.}$$

(from derivative of average electrostatic potential energy).



Consistent with the virial theorem.

→ Validity criterion of the Born-Oppenheimer adiabatic approximation

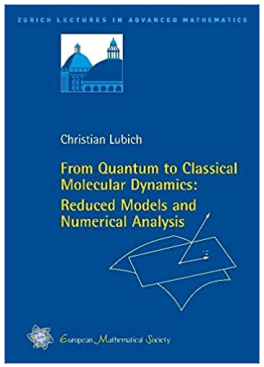
Electronic time scale $\sim\varepsilon$ vibrational time scale (except a crossings…)

They are inconsistent with Lubich ’08, p. 27 [DOI: 10.4171/067],

$$E\sim\varepsilon, \qquad Q\sim\sqrt{\varepsilon}, \qquad P\sim\frac{1}{\sqrt{\varepsilon}}, \qquad v\sim\varepsilon\sqrt{\varepsilon}$$

$$E\sim 1, \qquad Q\sim 1, \qquad P\sim\frac{1}{\varepsilon}, \qquad v\sim\varepsilon \text{ ???}$$

$$t\sim\frac{1}{\varepsilon}\rightarrow\tau\sim 1\text{: OK}$$



We are interested in solutions to the Schrödinger equation of bounded energy, and in particular of bounded kinetic energy

$$\langle\Psi\,|\,-\frac{\varepsilon^2}{2}\Delta_x\,|\,\Psi\rangle=\frac{1}{2}\,\|\varepsilon\nabla_x\Psi\|^2=\mathcal{O}(1)\,.$$

For a wavepacket $e^{ip\cdot x}a(x)$ this condition corresponds to a momentum $p\sim\varepsilon^{-1}$ and hence to a velocity $v=p/M\sim\varepsilon$. Motion of the nuclei over a distance ~ 1 can thus be expected on a time scale ε^{-1}. We therefore rescale time

$$t\rightarrow t/\varepsilon\,,$$

so that with respect to the new time nuclear motion over distances ~ 1 can be expected to occur at time ~ 1. The molecular Schrödinger equation in the rescaled time then takes the form

$$i\varepsilon\frac{\partial\Psi}{\partial t}=H^\varepsilon_{\rm mol}\Psi\,. \tag{2.9}$$

The Schrödinger equation (2.6) for the nuclei becomes

$$i\varepsilon\frac{\partial\psi}{\partial t}=H^\varepsilon_N\psi \quad\text{with}\quad H^\varepsilon_N=-\frac{\varepsilon^2}{2}\Delta_x+E+\varepsilon B_1+\varepsilon^2B_2\,, \tag{2.10}$$

$$B_1=\mathrm{Im}\,\langle\nabla_x\Phi\,|\,\Phi\rangle_{L^2_y}\cdot p\,,\qquad B_2=\frac{1}{2}\,\|\nabla_x\Phi\|^2_{L^2_y}\,,$$

with $p=-i\varepsilon\nabla_x$. We are interested in solutions over times $t=\mathcal{O}(1)$.

→ Does not seem compatible with small energy scale, but same semiclassical equations…

Numerical considerations

Practical simulations of quantum dynamics, for example with MCTDH + QVC Hamiltonian

→ often with dimensionless normal coordinates, $\mathcal{Q} = Q/\beta$

→ values close to 1 (both Q and β are $\sim\sqrt{\varepsilon}$): numerically convenient

→ always with time in atomic units: significant $t\sim\frac{1}{\varepsilon} \approx$ 100 a.u. $\approx$ 2 fs ($\tau\sim 1$)

→ time step for numerical integration $t \to t + \delta t$: typically, $\delta t\sim\frac{1}{\sqrt{\varepsilon}} \approx$ 10 a.u. $\approx$ 0.2 fs

→ final time: $t = T \approx 10^4$ to 10^5 a.u. $\approx$ 200 to 2000 fs (100 to 1000 semiclassical τ)

To go beyond

Anharmonicity effects and/or coupled electronic states (breathing, branching…)

First- and second-order nonadiabatic couplings [see Teufel, Lubich, …] (delta parameter)

System-bath partition (modes with distinct scales because different values of k and μ)

Influence of atomic numbers (hidden in k) together with masses?

Initial condition / dynamical regime (actual width *vs.* natural width *vs.* epsilon…)