Molecular quantum dynamics: Syllabus

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I. INTRODUCTION (CANNOT BE CHOSEN AS A FOCUS AREA, BUT MAY BE ALSO EXAMINED IN THE GENERAL AREA)

Reading: Lecture notes 1-2; Tannor 1, A.1

A. Exact quantum dynamics

Photoabsorption spectrum by a single dynamics calculation

B. Semiclassical dynamics

Bohr model of the H atom
Radial distribution function of I_2

C. Operators, observables, Dirac notation

Change of representation, position state, momentum state, Dirac delta function, time-dependent Schrödinger equation

II. EXACT METHODS TO SOLVE THE TDSE

Reading: Tannor 1, 2, 3.1-3.3, 4.1; S&R 4.1, 4.2

A. Basis set solution: Time-independent H

$$\psi(q,t) = \sum_n c_n \varphi_n(q) e^{-iE_n t/\hbar}$$

B. Basis set solution: Time-dependent H

$$
\begin{aligned}
H(t) &= H_0 + V(t) \\
\psi\left(q,t\right) &= \sum_n c_n(t)\varphi_n(q)e^{-iE_nt/\hbar} \\
\dot{c}_k(t) &= -\frac{i}{\hbar}\sum_n e^{i\omega_{kn}t}V_{kn}(t)c_n(t)
\end{aligned}
$$

C. Basis set solution in a general time-dependent nonorthogonal basis: Time-dependent H

overlap matrix

nonadiabatic coupling matrix

Hamiltonian matrix

III. TIME DEPENDENCE IN QM

Stationary state, wave packet, expectation value

A. Free-particle wave packet

particular solution

$$
\begin{aligned}
\psi(q,t) &= e^{i(kq-\omega t)} \\
p = \hbar k, &\quad E = \hbar\omega, \quad \omega(k) = \frac{\hbar k^2}{2m}
\end{aligned}
$$

de Broglie relation, Einstein relation, dispersion relation, phase velocity, group velocity

general solution

$$\psi(q,t) = \frac{1}{\sqrt{2\pi}}\int a(k)e^{i(kq-\hbar k^2t/2m)}dk$$

How to find $a(k)$?

center of the wavepacket, dispersion of the wavepacket

B. Quantum dynamics of a coupled two-level system

As in homework.

Rabi frequency

transition probability

C. Commutator and its properties

skew-symmetry, Jacobi identity

D. Ehrenfest theorem

Statement and proof.

E. Conservation of energy and norm by TDSE

Statement and proofs.

IV. GAUSSIAN WAVE PACKETS

general properties of a Gaussian wavepacket

$$\psi(x,t) = \exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}\alpha_t\left(x-q_t\right)^2 + p_t(x-q_t) + \gamma_t\right]\right\}$$

center, width, Heisenberg uncertainty relation

minimum uncertainty wavepacket

Gaussian free particle

GWP in a linear potential; general features

GWP in a quadratic potential; general features

energy of a coherent state

thawed Gaussian approximation

coherent state of a harmonic oscillator

frozen Gaussian approximation

V. REVIEW OF CLASSICAL MOLECULAR DYNAMICS

Reading: Lecture notes 3-4; Tannor 5.1, 5.2, 10.1.1

A. Newtonian mechanics

Newton's equation of motion

$$m\frac{d^2}{dt^2}\mathbf{q} = -\nabla V(\mathbf{q})$$

B. Lagrangian mechanics

variational principle

principle of least action (of stationary action)

Lagrangian $L\left(q, \dot{q}, t\right) := T(q, \dot{q}) - V(q, t)$

action $S\left[q(t)\right] := \int_0^t L(q, \dot{q}, \tau)\, d\tau$

Euler-Lagrange equations of motion

$$\frac{\partial L}{\partial q} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}} = 0$$

C. Hamiltonian mechanics

momentum $p := \frac{\partial L(q,\dot{q},t)}{\partial \dot{q}}$

Hamiltonian $H(q, p, t) := \dot{q}p - L(q, \dot{q}, t)$

energy

Hamilton's equations of motion

$$\dot{q} = \frac{\partial H}{\partial p} \quad \text{and} \quad \dot{p} = -\frac{\partial H}{\partial q}$$

molecular dynamics

Hamiltonian in polar coordinates

$$H = \frac{p_r^2}{2\mu} + \frac{p_\varphi^2}{2\mu r^2} + V(r)$$

**Not this year:* nondiagonal Hamiltonian for photodissociation of CO_2 (bond lengths coordinates)

$$R_1 = x_3 - x_2 \quad \text{and} \quad R_2 = x_2 - x_3$$

Not this year: Jacobi coordinates: How are they defined for atoms A, B, C?

D. *Not this year: Basics of Hamilton-Jacobi mechanics

variation of action with free endpoints

relation of action to momenta (initial point: q_i, p_i; final point at time t: q, p):

$$p = \frac{\partial S(q_i, q, t)}{\partial q} \quad \text{and} \quad p_i = -\frac{\partial S(q_i, q, t)}{\partial q_i}$$

Hamilton-Jacobi equation

$$-\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + V(q)$$

E. Phase space

configuration space and phase space

phase portrait: free particle $\approx$ ideal gas, SHO $\approx$ bond stretch, pendulum $\approx$ hindered rotation

stable/unstable fixed point, separatrix, libration

Bohr-Sommerfeld quantization rules: SHO

Liouville's theorem

VI. CONNECTIONS BETWEEN CLASSICAL AND QUANTUM MECHANICS

A. Commutator and its properties

skew-symmetry, Jacobi identity

B. Ehrenfest theorem

Statement and proof.

C. Conservation of energy and norm by TDSE

Statement and proofs.

D. Poisson bracket and its properties

Jacobi identity

skew-symmetry

Hamilton's equations in terms of Poisson brackets

E. Bohr-Sommerfed quantization rules

F. Wigner representation of a wave function

$$\rho_W(q,p) := \frac{1}{2\pi\hbar}\int \psi(q-s/2)\psi^*(q+s/2)e^{ips/\hbar}ds$$

properties of the Wigner function

$$\int \rho_W(q,p)\,dq = |\psi(p)|^2$$
$$\int \rho_W(q,p)\,dp = |\psi(q)|^2$$

Wigner function of a GWP

GWP in a SHO

VII. APPROXIMATE METHODS TO SOLVE TDSE

Reading: Lecture notes; S&R 4.3.1-4.3.3, 4.5.1, 4.5.2, 4.5.4; Tannor 9.4.1

A. Sudden approximation

$$c_n = \langle\varphi_n|\psi(0)\rangle = \int \varphi_n^*(q)\psi(q,0)dq,$$
$$|\psi(t)\rangle = \sum_n c_n e^{-iE_nt/\hbar}|\varphi_n\rangle$$

Franck-Condon transition

B. Adiabatic approximation

nth eigenstate of H_0 remains nth eigenstate of $H(t)$ for all t

$$H(t)\psi_n(q,t) = E_n(t)\psi_n(q,t)$$

quantum adiabatic theorem

Born-Oppenheimer approximation

C. Time-dependent perturbation theory (TDPT)

first order TDPT, $c_k(t=0) = \delta_{km}$:

$$P_{m\to k}(t) = |c_k^{(1)}(t)|^2 = \frac{1}{\hbar^2}\left|\int_0^t V_{km}(\tau)e^{i\omega_{km}\tau}d\tau\right|^2$$

higher order TDPT

$$\dot{c}_k^{(j)}(t) = -\frac{i}{\hbar}\sum_n e^{i\omega_{kn}t}V_{kn}(t)c_n^{(j-1)}(t)$$

1. *Not this year: *Collision induced excitation of a diatomic molecule*

collision cross section $\sigma_{m\to k}$, microcanonical rate constant $k_{m\to k}(E_0)$, thermal rate constant $k_{m\to k}(T)$

2. *TDPT for a constant potential V*

$$P_{m\to k}(t) = |V_{km}|^2 \frac{\sin^2 \frac{(E_k-E_m)T}{2\hbar}}{\left(\frac{E_k-E_m}{2}\right)^2}$$

Fermi's Golden Rule

$$w_T = \frac{P_T}{T} = \frac{2\pi}{\hbar}\rho(E_m)\left\langle|V_{km}|^2\right\rangle$$

3. *TDPT for a periodic potential $V(t) = U\cos\omega t$*

electric dipole approximation

FGR for a periodic potential

$$w_T = \frac{P_T}{T} = \frac{2\pi}{\hbar}\rho(E_m \mp \hbar\omega)\left\langle |U_{km}|^2 \right\rangle$$

absorption

stimulated emission

spontaneous emission

VIII. CORRELATION FUNCTIONS AND SPECTRA AND NUMERICAL METHODS TO SOLVE THE TDSE

Reading: Lecture notes; S&R 5.4.1, 5.4.2, 5.4.9; Tannor 6.1, 6.2, 11.6.5, 11.7.1

electric dipole moment

Franck-Condon overlap

spectrum as a Fourier transform of the wavepacket autocorrelation function

features of spectra and autocorrelation functions: recurrences, decays, peak spacings, peak widths

Examples: direct photodissociation, harmonic system

Fourier transform pairs: 3 examples

inverse Fourier transform

$$\tilde{f}(k) := \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(x)e^{-ikx}dx.$$

$$f(x) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \tilde{f}(k)e^{+ikx}dk.$$

preservation of inner product

$$\langle f, g\rangle = \left\langle \tilde{f}, \tilde{g} \right\rangle$$

Fourier convolution theorem

$$\widetilde{fg} = \frac{1}{\sqrt{2\pi}}\tilde{f} * \tilde{g}$$

A. Numerical methods to solve TDSE

discretization of the wave function

discrete Fourier transform (DFT)

fast Fourier transform (FFT)

B. Fourier method

algorithm?

C. Split operator method

algorithm?
particle in a magnetic field

D. *Not required: Second-order methods

Second-order split-operator algorithm
First-order implicit Euler method
Second-order trapezoidal rule

IX. PATH INTEGRAL FORMALISM

Reading: Lecture notes; Tannor 10.1.1, 10.1.2, 10.2

A. Feynman path integral propagator

quantum propagator
free particle propagator
short-time propagator
long-time propagator
Feynman path integral propagator

B. Quantum thermodynamics

thermal energy of the simple harmonic oscillator (SHO)
classical thermal energy obtained by equipartition theorem and by classical MD
quantum thermal energy obtained from the partition function
partition function as a trace of the Boltzmann operator $Q = \mathrm{Tr}\, e^{-\beta \hat{H}}$

thermal energy from partition function $E(\beta) = -\frac{\partial}{\partial\beta}\log Q(\beta)$

$$Q_{\rm PI}(\beta, N) = \left(\frac{mN}{2\pi\hbar^2\beta}\right)^{N/2} \int dq_1 \cdots \int dq_N \exp\left(-\beta V_{\rm eff}\right)$$

$$V_{\rm eff} = \frac{mN}{2\hbar^2\beta^2}\sum_{j=1}^{N}(q_j - q_{j-1})^2 + \frac{1}{N}\sum_{j=1}^{N} V(q_j)$$

Interpretation: quantum thermodynamics $\Leftrightarrow$ quantum dynamics in imaginary time

$$e^{-\beta\hat{H}} \Leftrightarrow e^{-i\hat{H}t/\hbar}$$

Interpretation: quantum thermodynamics $\Leftrightarrow$ classical thermodynamics of a polymer chain

Why PI useful for imaginary time dynamics and not so for real dynamics?

beads

estimator for energy

PIMC, PIMD

virial vs. thermodynamic estimator for energy

X. INTRODUCTION TO SEMICLASSICAL METHODS

Reading: Lecture notes; Tannor 5.2, 10.3

Bohr-Sommerfeld quantization rules: SHO and hydrogen atom (see also Question 1)

$$\oint p\, dq = nh$$

A. Gaussian wavepacket methods

GWP in a linear potential: general features

GWP in a quadratic potential: general features

frozen Gaussian approximation

thawed Gaussian approximation

B. Time-dependent WKB approximation

Ansatz:

$$\psi(q,t) = A(q,t)\exp\left[\frac{i}{\hbar}S(q,t)\right]$$

Result: Hamilton-Jacobi equation, Bohm potential, continuity equation

$$-\frac{\partial S}{\partial t} = \frac{(\nabla S)^2}{2m} + V(q) - \frac{\hbar^2}{2m}\frac{\nabla^2\rho^{1/2}}{\rho^{1/2}},$$
$$\frac{\partial}{\partial t}\rho + \nabla\cdot\left(\rho\frac{\nabla S}{m}\right) = 0$$

Bohmian dynamics

Semiclassical approximation

C. *Not required: Semiclassical Van Vleck propagator

Quantum propagator

$$K(q'',q';t) := \left\langle q'' \left| e^{-iHt/\hbar} \right| q' \right\rangle,$$
$$\psi(q'',t) = \int K(q'',q';t)\,\psi(q',0)\,dq'.$$

Van Vleck-Gutzwiller propagator

$$K_{\mathrm{SC}}(q'',q';t) = (2\pi i\hbar)^{-D/2}\sum_j A_j e^{iS_j/\hbar - i\pi\nu_j/2},$$
$$A_j = \sqrt{\left|\det\frac{\partial^2 S_j}{\partial\mathbf{q}''\partial\mathbf{q}'}\right|}$$

Van Vleck determinant

Maslov index ν_j

Derivation of the Van Vleck propagator from the short-time quantum propagator

D. Wigner function

See question on review of classical mechanics.

E. Ehrenfest theorem

Proof?

$$\frac{d\langle q\rangle}{dt} = \frac{\langle p\rangle}{m}$$
$$\frac{d\langle p\rangle}{dt} = -\left\langle \frac{\partial V}{\partial q} \right\rangle$$

XI. INTERACTION OF MOLECULES WITH ELECTROMAGNETIC FIELDS

Lagrangian for the interaction of a particle with electromagnetic field (brief justification, does not have to as thorough as I did in the lecture or lecture notes)

$$L(\mathbf{x}, \mathbf{v}, t) = \frac{1}{2}mv^2 - e\,\varphi(\mathbf{x}, t) + e\,\mathbf{v}\cdot\mathbf{A}(\mathbf{x}, t) \tag{1}$$

Derivation of the Lorentz force

Derivation of the corresponding Hamiltonian

$$H(\mathbf{x}, \mathbf{p}) = \frac{1}{2m}\left(\mathbf{p} - e\mathbf{A}\right)^2 + e\varphi.$$

Gauge transformations

$$\mathbf{A} \mapsto \mathbf{A}' := \mathbf{A} + \nabla\chi(\mathbf{x}, t) \quad \text{and} \quad \varphi \mapsto \varphi' := \varphi - \frac{\partial\chi(\mathbf{x}, t)}{\partial t}$$

Gauge invariance of electric and magnetic fields

Coulomb gauge

$$\nabla\cdot\mathbf{A} = 0$$

Weyl Gauge

$$\varphi = 0 \quad \text{(four sources at infinity)}$$

Long-wavelength approximation: $\mathbf{A}\,(\mathbf{x}, t) \approx \mathbf{A}\,(t)$

Derivation of the electric-dipole approximation

$$H = \frac{p^2}{2m} - \boldsymbol{\mu}\cdot\mathbf{E}(t)$$

A. *_Not this year_: Molecular Hamiltonian in adiabatic basis

XII. TIME-DEPENDENT VARIATIONAL APPROXIMATION

Time-dependent variational principle: statement

Conservation of energy and norm: Statement and proofs

Time-dependent Hartree approximation: Statement and derivation

mean-field Hamiltonian

*Not this year: Ehrenfest dynamics