# INTRODUCTION TO MODELLING
## from quantum to classical mechanics

Herman J.C. Berendsen
Biophysical Chemistry, University of Groningen, the Netherlands
Groningen Institute for Biosciences and Biotechnology (GBB)

CSC, Espoo

**Lecture 1, Tuesday 3 Feb, 2004**

The real world consists of nuclei, electrons and photons, interacting through electromagnetic and sometimes gravitational forces. They obey Diracs and Schrödingerss equations. At this level our knowledge is complete, but useless if we wish to study the folding of a protein or the binding of a ligand to a protein. The basic approximation that allows the study of realistic many-particle systems is the assumption that nuclei behave classically. How valid is this approximation?

But even when classical mechanics is correct, we need to make simplifications in order to treat large systems and long time scales. This is done by averaging over less important degrees of freedom, resulting in *stochastic* dynamics.

A survey of the whole hierarchy of simulation methods from quantum mechanics to macroscopic dynamics will be given first, Next we shall consider the classical approximation. Where does it go wrong? A fundamental discrepancy between quantum mechanics and classical mechanics that poses still unsolved problems is that the classical notion of a trajectory of particle positions evolving in time, does not exist in quantum mechanics.

# WHY QUANTUM MECHANICS?-1

---

Particles are described by a complex wave function $\Psi(\boldsymbol{r},t)$ that obeys the Schrödinger equation:

$$i\hbar\frac{\partial\Psi}{\partial t}=\hat{H}\Psi=-\frac{\hbar^2}{2m}\nabla^2\Psi+V(\boldsymbol{r},t)\Psi$$

The value of $\Psi*(\boldsymbol{r},t)\Psi(\boldsymbol{r},t)$ gives the probability of finding the particle at position $\boldsymbol{r}$ at time $t$.

For every observable $A$ an operator $\hat{A}$ exists. Operators are formed by replacing the momentum $p=mv$ by $-i\hbar\nabla$. The expectation value of an observable $A$ is

$$\langle A\rangle=\int\Psi*\hat{A}\Psi\,d\boldsymbol{r}$$

---

A free particle that starts out at $t=0$ with a Gaussian distribution with standard deviation $\sigma_0$, broadens in time with increasing width

$$\sigma(t)=\sigma_0\sqrt{1+\frac{\hbar^2t^2}{4m^2\sigma_0^4}}$$

The narrower it starts, the faster it spreads. A particle does not remain localized, unless it is subjected to a restraining potential, in which case it will evolve into a stationary bound state.

# WHY QUANTUM MECHANICS?-2

How broad are particles, compared to the distance to neighboring particles?

Consider a (nearly) classical particle with mass $m$ in an equilibrium system at temperature $T$, where it will have a Maxwellian velocity distribution (in each direction) with $\langle p^2 \rangle = mk_BT$. This uncertainty in momentum implies that the particle's *width* $\sigma_x$, i.e., the standard deviation of its wave function distribution, will exceed the value prescribed by Heisenberg's uncertainty principle $\Delta x \Delta p > \hbar/2$:

$$\sigma_x \geq \frac{\hbar}{2\sqrt{mk_BT}}.$$

There will be quantum effects if the forces acting on the particle vary appreciably over the width of the particle. A critical quantum width would be 0.1 Å.

| | m(u) | 10 K | 30 K | 100 K | 300 K | 1000 K |
|---|---|---|---|---|---|---|
| e | 0.000545 | **47** | **27** | **15** | **8.6** | **4.7** |
| H | 1 | **1.1** | **0.64** | **0.35** | **0.20** | **0.11** |
| D | 2 | **0.78** | **0.45** | **0.25** | **0.14** | 0.078 |
| C | 12 | **0.32** | **0.18** | **0.10** | 0.058 | 0.032 |
| O | 16 | **0.28** | **0.16** | 0.087 | 0.050 | 0.028 |
| I | 127 | 0.098 | 0.056 | 0.031 | 0.018 | 0.010 |

# WHY QUANTUM MECHANICS?-3

## Conclusions

**Electrons** are fully quantum-mechanical in all cases.

**Hydrogen** and **deuterium** atoms are suspect at 300 K. Hydrogen transfer (e.g. over hydrogen bond) may well be determined by quantum effects (*tunneling*).

**Heavier atoms** will be largely classical, at least at normal temperatures. Their quantum effects can be treated by *quantumcorrections*.

For *steep intermolecular potentials* even heavy atoms at room temperature show essential quantum effects: bond vibrations in molecules. The criterium for classical behaviour is here that vibrational frequencies should not exceed $k_B T/h$, which at $T = 300$ K amounts to about 6 THz, or a wave number of about 200 cm$^{-1}$. Quantum corrections are possible in the harmonic approximation.

# MACROSCOPIC QUANTUM EFFECTS-1

Sure signs of quantum effects: dependence of thermodynamic quantities on atomic mass:

**Critical point characteristics**

| | $T_c$(K) | $p_c$(bar) | $V_c$ (cm$^3$ mol$^{-1}$) |
|---|---|---|---|
| $^4$He | 5.20 | 2.26 | 57.76 |
| $^3$He | 3.34 | 1.15 | 72.0 |
| $H_2$ | 33.18 | 12.98 | 66.95 |
| HD | 35.9 | 14.6 | 62.8 |
| $D_2$ | 38.3 | 16.3 | 60.3 |
| $H_2O$ | 647.14 | 220.64 | 56.03 |
| $D_2O$ | 643.89 | 216.71 | 56.28 |

# MACROSCOPIC QUANTUM EFFECTS-2

## Various properties of normal and heavy water

| | $H_2O$ | $D_2O$ |
|---|---|---|
| melting point (°C) | 0 | 3.82 |
| boiling point (°C) | 100 | 101.4 |
| temperature of max. density (°C) | 3.98 | 11.19 |
| vaporization enthalpy at 3.8 °C (kJ/mol) | 44.8 | 46.5 |
| molar volume at 25 °C ($\mathrm{cm}^3$/mol) | 18.07 | 18.13 |
| molar heat capacity at 25 °C ($\mathrm{J\,K^{-1}\,mol^{-1}}$) | 74.5 | 83.7 |
| ionization constant $-\log[K_w/(\mathrm{mol}^2\,\mathrm{kg}^{-1}]$ at 25°C | 13.995 | 14.951 |

Effects are small but not negligible. In simulations force fields are used that are adjusted to measured properties, and thus include average quantum corrections.

# FROM QUANTUM TO CLASSICAL-1

Can we derive classical equations of motion from the Schrödinger equation?

**Ehrenfest (1927)**:
Consider one-dimensional case of a particle of mass $m$ with position $x$ and momentum $p = m\ddot{x}$. The classical equations of Newton are

$$\frac{dx}{dt} = \frac{p}{m}$$

$$\frac{dp}{dt} = -\frac{dV(x)}{dx}$$

Position and momentum of a quantum particle must be interpreted as the expectation of $x$ and $p$. The classical force would then be the value of the gradient of $V$ taken at the expectation value of $x$. So we ask whether

$$\frac{d\langle x\rangle}{dt} ? =? \frac{\langle p\rangle}{m}$$

$$\frac{d\langle p\rangle}{dt} ? =? -\left(\frac{dV}{dx}\right)_{\langle x\rangle} .$$

Ehrenfest showed that indeed

$$\frac{d\langle x\rangle}{dt} = \frac{\langle p\rangle}{m}$$

but that

$$\frac{d\langle p\rangle}{dt} = -\langle\frac{dV}{dx}\rangle.$$

# FROM QUANTUM TO CLASSICAL-2

The momentum change is the expectation value of the force, not the force at the expectation value of $x$! When the force is constant, the motion of $x$ and $p$ is classical. Expanding the potential in a Taylor series, we see that the leading correction term on the force is proportional to the second derivative of the force times the variance of the wave packet:

$$\langle \frac{dV}{dx} \rangle = \left(\frac{dV}{dx}\right)_{\langle x \rangle} + \frac{1}{2!}\left(\frac{d^3V}{dx^3}\right)_{\langle x \rangle} \langle (x - \langle x \rangle)^2 \rangle + \dots$$

The motion is classical if the gradient of the force does not vary much over the quantum width of the particle. This is true even for electrons in macroscopic fields, as they occur in accelerators and in dilute or hot plasmas; this is the reason that hot plasmas can be treated with classical equations of motion, as long as the electromagnetic interactions are properly incorporated. For electrons near point charges the force varies enormously over the quantum width and the classical approximation fails completely.

# THE BORN-OPPENHEIMER APPROXIMATION

---

The **Born-Oppenheimer** approximation assumes that electrons are *infinitely fast* with respect to the nuclei, so that they immediately follow the change in nuclear positions. This means that the nuclear coordinates are *parameters* in the Schrödinger equation for the electrons:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$

with

$$\Psi = \Psi(\boldsymbol{r}, t; \boldsymbol{R})$$

and

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2_{\boldsymbol{r}}\Psi + V(\boldsymbol{r}; \boldsymbol{R})\Psi$$

For every configuration of nuclei there are a number of *steady-state solutions* for the electronic Schrödinger equation:

$$\Psi_n(\boldsymbol{r}, t) = \Phi_n(\boldsymbol{r}) \exp(iE_n/\hbar)$$

$$\hat{H}\Phi_n = E_n(\boldsymbol{R})\Phi_n$$

Generally only the ground state with energy $E_0(\boldsymbol{R})$ is of interest.

**Quantum chemistry**: Solutions by *Hartree-Fock methods*: molecular orbitals by linear combination of atomic orbitals, or by *Density Functional Theory* (for the ground state only).

# ELECTRONIC MOTION IN THE FIELD OF MOVING NUCLEI

---

We wish to consider electrons as quantum particles and nuclei as classical particles. Is this possible?

**Approaches**:

1. Separate quantum and classical degrees of freedom,
2. Solve quantum dynamics in time-dependent field - by numerical integration of wave function on grid - by evolution of wave function,
3. Solve simultaneously classical equations of motion

**Major question**: *What is the back-reaction from quantum system on classical d.o.f.?*

*Back-reaction* = force due to quantum d.o.f. on classical d.o.f.

This determines the classical dynamics and thus the time-dependence of the field in which the quantum system evolves.

# BACK REACTION

**Cases**:

a. **B-O approximation is valid**. Quantum system is in ground state; energy gap with excited states is high. System remains in ground state. Back reaction force is average over ground state.

b. **B-O approximation violated**. System may bifurcate into different quantum branches. Solution requires consideration of quantum character of nuclear motion. Approximations:

   - nuclear motion is considered in quantum approximation (e.g. in reactive collision theory) [restricted to a few nuclei]
   - classical system moves on potential energy surface of average quantum evolution [sometimes correct]
   - classical system chooses stochastically between potential energy surfaces of different quantum branches (surface hopping) [misses quantum coherence of different branches]
   - multistate evolution: simultaneous evolution of several classical trajectories [field is in progress]

# MOTION IN NON-STATIONARY FIELDS-1

---

The time-dependent Schrodinger equation

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar}\hat{H}\Psi = -\frac{i}{\hbar}(\hat{K}+\hat{V})\Psi$$

can *formally* be solved as

$$\Psi(t) = \exp\left(-\frac{i}{\hbar}\int_0^t [\hat{K}+\hat{V}(t')]\,dt'\right)\Psi(\boldsymbol{r},0)$$

For small time step:

$$\Psi(t+\Delta t) = \exp\left(-\frac{i}{\hbar}\int_t^{t+\Delta t}[\hat{K}+\hat{V}(t')]\,dt'\right)\Psi(\boldsymbol{r},t)$$

$$\approx \exp\left[-\frac{i}{\hbar}\left(\hat{K}+\hat{V}(t+\frac{1}{2}\Delta t)\right)\Delta t\right]\Psi(\boldsymbol{r},t)$$

$$\approx \exp\left(-\frac{i\hat{K}\Delta t}{2\hbar}\right)\exp\left(-\frac{i\hat{V}(t+\frac{1}{2}\Delta t)\Delta t}{\hbar}\right)\exp\left(-\frac{i\hat{K}\Delta t}{2\hbar}\right)\Psi(\boldsymbol{r},t)$$

(Trotter-expansion)

V-part is easy in real space; K-part is easy in reciprocal space. Application: (solvated electron) Selloni et al., Phys.Rev.Lett. **59** (1987) 823.

# MOTION IN NON-STATIONARY FIELDS-2

If the nuclei move, the Schrödinger equation gets an extra term:

$$\frac{\partial \Psi}{\partial t} = -\frac{i}{\hbar}\hat{H}\Psi + \frac{d\boldsymbol{R}}{dt} \cdot \frac{\partial \Psi}{\partial \boldsymbol{R}}$$

The operator $\partial/\partial\boldsymbol{R}$ is called the *non-adiabatic coupling vector operator*.

In the limit $d\boldsymbol{R}/dt \rightarrow 0$ the time-independent solution is correct, but for finite $d\boldsymbol{R}/dt$ excited states, selected by the non-adiabatic coupling vector operator, will mix in with a rate proportional to $d\boldsymbol{R}/dt$.

Method to solve the adiabatic ground state by DFT, given positions of nuclei, on the fly is the ab initio molecular dynamics of Car and Parrinello: R. Car and M. Parrinello, Phys.Rev.Lett. 55 (1985) 2471.

# MOTION IN NON-STATIONARY FIELDS-3

Methods to include excited states (*non-adiabatic dynamics*) involve the mixing-in of other states. When two states cross, or are near to each other, the system will continue in one of the states. Full solution would require quantum character of nuclei.

Example: **Fate of excited state**

*Rhodopsin photo-isomerisation*

retinal 11-*cis* → *trans* conversion via excited state, within 200 fs.

[B. Hahn and G. Stock, J. Phys. Chem. **B 104** (2000) 1146-1149]

**model**: quantum wave packet described on basis set product wave functions of
150 rotor states in dihedral angle $\phi$
$\times$ 24 harmonic oscillator states $\perp \phi$
$\times$ 3 electronic states
fitted to spectroscopic data

# MOTION IN NON-STATIONARY FIELDS-4

Example: **Fate of excited state**

*Photo-active Yellow Protein photo-isomerisation*

coumaric acid chromophore *trans* → *cis* conversion via excited state, within 250 fs.