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Brief Summary of Tutorial I and of the Next Task

- Objective of large-scale simulations is to predict and interpret the properties of real material systems
- A lot of progress can be made toward that objective by Molecular Dynamics, which is basically the solution of Newton’s equations for $N_n =$ thousands to millions of particles interacting by a potential $V(R) \equiv V(R_1, R_2, R_3 \ldots R_{N_n})$
- All the chemical binding information about the system is contained in the potential $V(R)$.
- Details of chemical binding are determined by the electrons in the system, so the potential $V(R)$ must be taking account of the electrons.
- We can fit a potential by forcing the simulation to have a collection of correct, i.e. experimental, values of a set of properties (crystal structure, cell constants, $P$ vs. $\Omega$, etc.). Such potentials are called empirical.
- But the goal is to predict material properties, that is, the outcome of experiments. So somehow we must derive the potential from the behavior of the electrons.
- Electrons obey Quantum Mechanics $\Rightarrow$ Next Task = summarize and review Quantum Mechanics
Quantum Mechanics

Quantum Mechanics - “QM” - will provide an essential ingredient to our simulations, the potential $V(R)$. In fact, it will provide the insight that, to a high level of approximation, the potential actually is the energy of the whole cloud of electrons when the nuclei are at the given positions $R$. Preview: this means that there should be more in the simulation than just the potential!

- Some notation: We’ll use a common (but not universal) notational convention for electrons because they are the particles of eventual interest. The position and momentum of the “i”th particle, mass $m_i$ in some fixed frame are

$$
\begin{align*}
    r_i &= \text{position vector} \\
    p_i &= \text{momentum vector}
\end{align*}
$$

Notice the lower case; in this convention upper case is for nuclear or ionic coordinates. For the most part we will summarize QM for one particle in 1D.

- QM came into being to explain many phenomena, mostly spectral. The questions include, why do atomic spectra have lines? (Look at a street light: if it uses mercury vapor its light is purple-white, if sodium vapor the light has a very orangeish tinge. At laboratory resolution, those turn out to be very strong lines in the spectra of those atoms.) Why do photoelectrons get emitted from a metal surface at and above only certain frequencies of incident light? Etc.

- These questions come down to asking why systems such as atoms can absorb and/or emit energy only at certain energies that correspond to certain frequencies:

$$
E_j = h\nu_j = \frac{h}{2\pi} (2\pi \nu_j) \equiv \hbar \omega_j
$$

$\hbar$ is introduced because the particular combination is very common in QM expressions.

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• Here $h$ is Planck’s constant. It has dimensions (obviously) of energy $\times$ time, or equivalently, angular momentum. Compared to a macroscopic angular momentum it is a very small number:

$$h = 6.626 \times 10^{-27}\text{erg-sec}$$

• Notice that there is a “classical limit”. If $\hbar$ is small compared to any characteristic angular momentum of the system, then that system can absorb (or emit) essentially any energy whatsoever.

• Eq. (1) is “overloaded” with meaning.
  1. For the photoelectric effect, it conveys the fact that the radiation field is quantized (light comes in energy packets called photons).
  2. For the blackbody radiation problem, it conveys the fact that the oscillators that generate the radiation have quantized energy levels that govern their emission. Notably there is a lowest level.
  3. For atomic spectra, it conveys the fact that the atom has quantized energy levels as well and that the absorption or emission of radiation is by energy differences between levels.

• Quantized energies can’t happen in CM without all sorts of arbitrary rigging of the game. Although a “solar system” model of the atom will give the right energies (Bohr model), there is something fundamentally wrong. Since the electrons are orbiting, then in CM they are subject to a radially inward acceleration of constant magnitude. But an accelerated charged particle in Classical Electromagnetism radiates continually and therefore loses energy continually so the orbit can’t be sustained. But it must be sustained to retain the energy level differences in the model.

• Since energy differences are critical, the focus turned away from forces. Note also: energy differences are not time-dependent, so effort turned away from dynamics to “stationary state” - system states that do NOT evolve with time.

• Desired: system energy difference before and after the transition $=$ energy of the incident (or emitted) radiation $\Rightarrow$ conservation of energy is important. After much intellectual struggle (mid 1890s - early 1930s) it
was clear that the Hamiltonian formulation of CM provides the cleanest route to quantization.

1. The way out of the CM vs. EM dilemma is to give up an unstated but fundamental postulate of CM.

2. In the Hamiltonian formulation, the unstated postulate is: “The classical state of a system is determined at all times by simultaneous exact knowledge of the positions and momenta of all the system particles.”

3. For macroscopic systems this assumption is sensible. But is it for atomic-scale systems? Heisenberg’s answer is “no”. Instead, adopt the uncertainty principle or postulate:

\[ \Delta x \Delta p_x \geq \hbar / 2 \]  

Here the uncertainties in a quantity \( Q \) are defined as

\[ (\Delta Q)^2 \equiv \bar{Q}^2 - (\bar{Q})^2 \]

This says we can know a lot about position at the cost of knowing little about momentum (implicitly therefore also little about K.E.) or conversely. How we calculate these mean values is the next task.

- Schrödinger’s formulation of QM of a single 1D particle in summary:

1. The probability density of finding a particle in the interval \( x \to x + dx \) at time \( t \) is given by

\[ |\Psi(x,t)|^2 \]  

where \( \Psi \) is called the state function or wave function. To make this a genuine probability distribution, it must be the case that

\[ \int_{-\infty}^{\infty} dx |\Psi(x,t)|^2 = 1 \]

assuming that the domain of the problem is the entire \( x \)-axis. This is called the normalization condition and the set of functions that satisfy this particular normalization are called \( L^2 \) functions. Notice that qualitatively such functions are bounded above and below and vanish as the argument goes to \( \pm \infty \). Comment: It is necessary to generalize this normalization to non-\( L^2 \) functions but we won’t do that here.
2. $\Psi$ is the solution of the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = H \Psi(x, t) \tag{4}$$

3. In eq. (4), $H$ is the Hamiltonian Operator which, in the Schrödinger form of QM, is formed from the CM Hamiltonian $\mathcal{H}$ by the following procedure:

$$\mathcal{H}(x, p) = \frac{p^2}{2m} + V(x)$$

$$p \rightarrow -i\hbar \frac{\partial}{\partial x}$$

$$\Rightarrow H(x, p) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \tag{5}$$

Comment: We have more symbol overload. This $V$ is NOT the same potential energy as the $V(R)$ considered at length in Tutorial I. This $V$ is to describe the potential energy involved with the QM system (at the moment, a single particle).

4. Thus $H$ is an operator that operates on $\Psi$:

$$H \Psi(x, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x) \Psi \tag{6}$$

5. Furthermore $p$ is an operator that does not commute with $x$. Suppose we have some general state $\Phi$, then

$$xp \Phi = -i\hbar x \frac{\partial \Phi}{\partial x}$$

$$px \Phi = -i\hbar \frac{\partial (x \Phi)}{\partial x} = -i\hbar \left[ \Phi + x \frac{\partial \Phi}{\partial x} \right] \tag{7}$$

Subtract the second of these from the first to get

$$(xp - px) \Phi = i\hbar \Phi$$

Since this relationship is true for all reasonable $\Phi$, we write

$$[x, p] := (xp - px) = i\hbar \tag{8}$$

Note that the order of operators and functions matters.
6. Stationary or time-independent states of the system are of the form

\[ \Psi_j(x,t) = \exp(-i\omega_j t)\psi_j(x) \]  \hspace{1cm} (9)

a fact that you can verify by substituting this expression into the T.D.S.E. eq. (4):

\[ i\hbar \frac{\partial \Psi_j(x,t)}{\partial t} = i\hbar \frac{\partial \exp(-i\omega_j t)\psi_j(x)}{\partial t} = \hbar\omega_j \exp(-i\omega_j t)\psi_j(x) \]

\[ H\Psi_j(x,t) = \exp(-i\omega_j t)H(x,p)\psi_j(x) \]

\[ \Rightarrow \exp(-i\omega_j t)H(x,p)\psi_j(x) \]  \hspace{1cm} (10)

These results yield the celebrated time-independent Schrödinger equation:

\[ H(x,p)\psi_j(x) = \hbar\omega_j\psi_j(x) \equiv E_j\psi_j(x) \]  \hspace{1cm} (11)

7. In order for \( \psi_j \) to be normalizable, we require that it be finite everywhere and vanish as \( x \to \pm\infty \).

8. The problem posed by the time-independent Schrödinger equation is called an “eigenvalue problem” (“eigen” a prefix from German meaning “proper”) and stationary states are called eigenstates.

9. To predict the measured value of an observable quantity call it \( Q \) in the Schrödinger formulation when the system is in a particular stationary state, we

- Form the operator \( Q \) that corresponds to the observable \( Q \).
- Calculate the “expectation value” of the operator for the given state

\[ \langle Q \rangle_j = \frac{\int_{-\infty}^{\infty} dx \psi_j^*(x)Q\psi_j(x)}{\int_{-\infty}^{\infty} dx \psi_j^*(x)\psi_j(x)} \]  \hspace{1cm} (12)

- Operators that correspond to observables must have real-valued eigenvalues. That means the operators must be Hermitian (pronounced almost “her-mis-shun”). In the Schrödinger formulation a Hermitian operator is one that obeys

\[ \int_{-\infty}^{\infty} dx \psi_j^*(x)Q\psi_j(x) = \int_{-\infty}^{\infty} dx (Q^*\psi_j^*(x))\psi_j(x) \]

10. From eqs. (12) and (11) it is evident that the energy eigenvalues are the expectation value of the Hamiltonian in the eigenstates:

\[ \langle H \rangle_j = \frac{\int_{-\infty}^{\infty} dx \psi_j^*(x)H\psi_j(x)}{\int_{-\infty}^{\infty} dx \psi_j^*(x)\psi_j(x)} \]
Exactly solvable stationary state problems are few in QM.

1. Free particle:

\[ V(x) = 0 \]

\[ -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_j}{\partial x^2} = E_j \psi_j \]  

Consider

\[ \psi_j(x) = A \exp(ikx) \]  

EVEN though this clearly is not normalizable. That problem can be handled (read up on the Dirac delta function if you are interested) and it isn’t an obstacle here; see below. This \( \psi_j \) is a solution if

\[ \frac{\hbar^2 k^2}{2m} = E_j \]  

Notice two things. First, there is no restriction on \( k \), that is, there isn’t any way to force a “j” labeling. But that’s a good thing, since this is a free particle. Second, the form of eq. (16) is suggestive of the notion that the momentum is quantized by \( p = \hbar k \) which is in fact one of the quantization conditions discovered very early in the development of QM.

2. Particle in a box:

In reality there are always boundaries. So we put the particle in a hard-walled box.

\[ V(x) = 0 \quad 0 < x < L \]

\[ V(x < 0) = V(x > L) = \infty \]  

The hard walls mean that the eigenfunction must go to zero at those points. Since we have the free particle solutions, eq. (15), we can try to make combinations of them that satisfy the boundary conditions and correspond to zero potential on \( 0 < x < L \). Let

\[ \psi_k(x) = A_k \cos(kx) + B_k \sin(kx) \]
At \( x = 0 \), \( \cos(kx) = 1 \), so \( A_k = 0 \). At \( x = L \)

\[
\sin(kL) = 0 \Rightarrow \\
kL = j\pi, j = 0, \pm 1, \pm 2, \pm 3, \ldots \\
k_j = j\pi/L, j = 0, \pm 1, \pm 2, \pm 3, \ldots
\]

(18)

We can omit \( j = 0 \) because it leaves a solution that is everywhere zero in the well and that can’t possibly yield a probability distribution. We can forget about one of the two signs because it only flips the sign of \( B \). Thus, take the positive integers. So

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_j}{\partial x^2} = E_j \psi_j \\
-\frac{\hbar^2}{2m}[-Bk_j^2 \sin(k_jx)] = B \sin(k_jx) \\
\frac{\hbar^2}{2m}k_j^2 = E_j \\
E_j = \frac{\hbar^2}{2m} \left( \frac{j\pi}{L} \right)^2 j = 1, 2, 3, \ldots
\]

(19)

The boundaries have induced a quantized energy spectrum. Notice the analogue with nodes on a string (e.g. guitar, violin) or in an organ pipe. Also notice that the energy of the ground state \( (j = 1) \) is just what you would get by assuming that the uncertainty \( \Delta x = L \):

\[
\Delta x \approx L \\
\Delta p_{\text{min}} = \frac{\hbar}{2\Delta x} = \frac{\hbar}{2L} \\
\Rightarrow \Delta E_{\text{min}} = \frac{(\Delta p)^2}{2m} = \frac{\hbar^2}{2m4L^2} = \frac{\hbar^2}{8mL^2} \\
E_1 = \frac{\hbar^2\pi^2}{2mL^2} = \frac{\hbar^2}{8mL^2}
\]

(20)

Still must normalize \( \psi_j \).

\[
1 = B_j^2 \int_0^L dx \sin^2[j\pi x/L] \\
B_j^{-2} = \frac{L}{\pi} \int_0^\pi du \sin^2(ju) \\
= \frac{L\pi}{\pi 2} = \frac{L}{2}
\]
3. Another important example is the QM simple harmonic oscillator. Still in 1D, the Hamiltonian operator is

\[
H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m \omega^2 x^2
\]

(22)

where the classical vibrational frequency is

\[
\omega = \sqrt{\frac{k}{m}}
\]

(23)

The time-independent Schrödinger equation therefore is

\[
-\frac{\hbar^2}{2m} \frac{\partial^2 \psi_j}{\partial x^2} + \frac{1}{2} m \omega^2 x^2 \psi_j = E_j \psi_j
\]

(24)

There are myriad ways to solve this differential equation subject to the boundary condition

\[
\lim_{x \to \pm \infty} \psi_j(x) = 0
\]

First focus on the ground state. The simplest way is to reflect on the fact that taking two derivatives of \(\psi_0\) must give back something proportional to \((x^2 - \text{constant})\psi_0\). Some thought will lead to the realization that

\[
\psi_0(x) = A_0 \exp[-\mu x^2]
\]

(25)

will work. Substituting this expression in eq. (24) leads to the requirement

\[
-\frac{\hbar^2}{2m} [-2\mu + 4\mu^2 x^2] + \frac{1}{2} m \omega^2 x^2 = E_0
\]

\[
\Rightarrow
\]

\[
-4\mu^2 \frac{\hbar^2}{2m} + \frac{1}{2} m \omega^2 = 0
\]

\[
2\mu \frac{\hbar^2}{2m} = E_0
\]

The last two lines give (work it out)

\[
\mu = \frac{m \omega}{2\hbar}
\]

\[
E_0 = \frac{1}{2} \hbar \omega
\]

(26)
If you now try $\psi_1(x) = A_1 x \exp[-\mu x^2]$ you will find $E_1 = \frac{3}{2} \hbar \omega$. You will also find that

$$\langle \psi_1 | \psi_0 \rangle \equiv \int_{-\infty}^{\infty} dx \psi_1^*(x) \psi_0(x) = 0$$

(27)

The two functions are “orthogonal”. (The angle bracket notation, which has more profound roots, is due to Dirac and is very useful. More on that below.) In fact, you can work out all the rest of the eigenvalues and eigenfunctions of the S.H.O. on the basis that each successive one must be orthogonal to the previous ones. This corresponds to Sturm’s theorem in differential equations. The result is

$$E_j = (j + \frac{1}{2}) \hbar \omega, \; j = 0, 1, 2, 3, \ldots$$

$$\psi_j(x) = A_j H_j(x) \exp[-\mu x^2]$$

(28)

where the $H_j$ are a set of orthogonal polynomials called Hermite (“her-meet”) polynomials.

As an exercise, try working out the mean value of $x$ and its uncertainty for the SHO.

4. Hydrogen atom:

Proton to electron mass ratio $\approx 1836$, so approximate the H atom as an immovable proton at the origin. Then recall exercise in Tutorial I and use $\nabla^2$ in spherical polar coordinates to get the Hamiltonian

$$H = -\frac{\hbar^2}{2m_e r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] - \frac{e^2}{r}$$

(29)

Aside about units: we switch to one form of atomic units:

$$\hbar = (2m_e) = e/\sqrt{2} = 1$$

(30)

These are called “Rydberg atomic units” and are most common in the physics literature. In these units lengths are in Bohr radii $a_0 \approx 0.52 \text{Å}$ and energies are in Rydbergs $1 \text{Ry} \approx 13.6 \text{eV}$. Quantum chemists typically use “Hartree atomic units” (which they often blissfully call “atomic units”), which are

$$\hbar = m_e = e = 1$$

(31)
These have the same length scale but the energy unit is the Hartree
1Hartree = 2Ry ≈ 27.2eV.

The standard approach is to recognize that the eigenfunctions of this
Hamiltonian factor ("separation of variables")

\[ \psi_j(r, \theta, \phi) = R_j(r) \Theta_j(\theta) \Phi_j(\phi) \]  (32)

This leads to three equations coupled by the separation constants \( \ell(\ell + 1) \)
and \( m \) when written in the conventional form:

\[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \left[ E + \frac{2}{r} - \frac{\ell(\ell + 1)}{r^2} \right] R = 0 \]

\[ \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Theta}{d\theta} \right) + \left[ \ell(\ell + 1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0 \]

\[ \frac{d^2\Phi}{d\phi^2} + m^2 \Phi = 0 \]  (33)

where the indexing of the eigenvalue and state has been suppressed for the
moment. It is standard textbook fare to show that the solutions to the last of
eqs. (33) are

\[ \Phi_m = \exp(\pm im\phi) \quad m = 0, 1, 2, \ldots \]  (34)

The next to last of eqs. (33) is a form of Legendre's equation and has
solutions known as associated Legendre functions, traditionally denoted
\( P^m_\ell(\cos \theta), -\ell \leq m \leq \ell \). The lowest one \( P^0_\ell \) is just a constant, the \( P^m_1 \) set is
proportional to \( \cos \theta \) or \( \sin \theta \) and so forth. The radial equation has solutions
in terms of associated Laguerre functions. You can find the lowest one
without that machinery by assuming that \( R \) is labeled by an energy
quantum number "\( j \)" and the number \( \ell \) which turns out to be the angular
momentum quantum number. Set \( \ell = 0 \) and try the solution

\[ R_{j\ell} = A_j \exp(-\gamma r) \]  (35)

It should work. You should read an elementary QM book’s chapter on the
simple H atom very carefully.
• Expansion in a Basis:
Putting aside mathematical niceties, generally the eigenfunctions of a Hamiltonian or other operator can be put into orthogonal and normalized form:

\[ \langle \psi_i | \psi_j \rangle \equiv \int_{x_1}^{x_2} dx \psi_i^*(x) \psi_j(x) = \delta_{ij} \]
\[ \delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \]

(36)

Such a collection of “orthonormal functions” usually forms what is called a complete set: on the same domain any reasonable function \( f(x) \) can be expanded in a linear combination of the orthonormal functions. Like this

\[ f(x) = \sum_{k=0}^{\infty} a_k \psi_k(x) \]
\[ a_k = \langle \psi_k | f \rangle = \int_{-\infty}^{\infty} dx \psi_k^*(x) f(x) \]

(37)

• Variation Principle:
Suppose we are given a Hamiltonian operator \( H \) that corresponds to a time-independent Schrödinger equation that we can’t solve analytically. How could we proceed to get an approximate solution that is guaranteed to converge on the exact result? The problem to be solved is

\[ H \psi_0 = E_0 \psi_0 \]

(38)

We assume a trial function \( \chi \) which, unless we are singularly unlucky, will have the implicit decomposition

\[ \chi = \psi_0 + \alpha \phi \]

(39)

In other words \( \chi \) is some unknown admixture of the desired eigenfunction and a residual that has nothing to do with \( \psi_0 \). Assume (introduce some more Dirac notation along the way)

\[ \langle \psi_0 | \phi \rangle = \int_{-\infty}^{\infty} dx \psi_0^*(x) \phi(x) = 0 \]

which gives specificity to the phrase “has nothing to do with \( \psi_0 \)”. Let \( \chi \) be normed as \( A = \langle \chi | \chi \rangle \). Expand the function \( \phi \) in a basis of the
eigenfunctions (admittedly unknown, but we know they exist) of $H$

$$\phi(x) = \sum_{j=1}^{\infty} b_j \psi_j$$  \hspace{1cm} (40)

Question - why wasn’t $\psi_0$ included? Form the expectation value of $H$ with respect to $\chi$

$$\frac{1}{A} \langle \chi | H | \chi \rangle = \frac{1}{A} \int_{-\infty}^{\infty} dx \chi^*(x) H \chi(x)$$

$$= \frac{1}{A} \int_{-\infty}^{\infty} dx \psi_0^*(x) H \psi_0(x) + \frac{\alpha}{A} \int_{-\infty}^{\infty} dx \psi_0^*(x) H \phi(x)$$

$$+ \frac{\alpha}{A} \int_{-\infty}^{\infty} dx \phi^*(x) H \psi_0(x) + \frac{\alpha^2}{A} \int_{-\infty}^{\infty} dx \phi^*(x) H \phi(x)$$

$$= \frac{E_0}{A} + \frac{\alpha}{A} (0 + 0) + \frac{\alpha^2}{A} \int_{-\infty}^{\infty} dx \phi^*(x) H \phi(x)$$

$$= \frac{1}{A} \left[ E_0 + \alpha^2 \sum_{j=1}^{\infty} b_j^2 E_j \right]$$

$$\geq \frac{E_0}{A}$$  \hspace{1cm} (41)

Some steps are left out. You need to think about them. What this proves is that I can vary $\chi$ and know that the lowest value that comes out is the exact eigenvalue. All other $\chi$s give upper bounds to $E_0$. 

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