CHE502 Chemical and Statistical Thermodynamics

Homework 2

URL: http://theo.ism.u-bordeaux.fr/PBopp/vistec.2020.2021

Equations able to describe the observations that we call 'quantum mechanics' (energy packages, interference, ie the particle-wave dualism) were developed by Erwin Schrödinger (1887-1961) and Werner Heisenberg (1901-1976). In the 1920ies the two gentlemen spent quite some time and effort squabbling among themselves who was right.
Eventually, it was demonstrated that both approaches are completely equivalent, one can use one or the other, it does not make any difference.

We will use mostly Schrödinger's description, because it is more intuitive (*even if you don't believe it*) and thus a bit easier for chemistry, but sometimes we will mix in some ideas coming from Heisenberg.

Schrödinger's theory is based on differential equations (similar to Newton's $m \cdot \frac{\partial^2}{\partial t^2} r = F$)
while Heisenberg's approach is based on 'Operators' and matrices

So when we speak about a 'Hamiltonian', or 'Hamilton Operator', (which we will call $\hat{H}$) in Schrödinger's equation, see later, we mix the two theories.

(*Shall we call it the Schrödinger-Heisenberg dualism 555? Schrödiberg ??? Heisendinger ???*)

Eigenvalue/eigenvector equations

This type of equation appears everywhere: mechanics (eg find the moments of inertia), electric circuits (find the resonance frequencies), spectroscopy, stability analysis in engineering, ... ,
and also in quantum mechanics
'Eigen....' in German means: "self-...", or "belonging to"; 'Eigentum' means property.

(*It is an old joke that Manfred Eigen (1927-2019) got the Nobel Prize (1967) for the eigenvector.
He got it for studying fast chemical reactions*)

Such eigenvalue/eigenvector equations are a bit peculiar because we need to find
two things from one equation: the eigenvalue(s) and the eigenvector(s) (typically there are many)

$\overline{M}$ is matrix (dimensions nxn), $\vec{a}$ is a n-dimensional vector, and λ is a scaler, then we try to find $\vec{a}$ and λ such that

$$\overline{M}\,\vec{a} = \lambda \cdot \vec{a} \quad \text{or} \quad \overline{M}\,\vec{a}_i = \lambda_i \cdot \vec{a}_i\ ,\ i = 1, 2...$$

A matrix multiplying a vector is a vector $\overline{M}\,\vec{a} = \vec{b}$,
so we are looking for the several vectors $\vec{a}_i$ that are not 'rotated' by $\overline{M}$,
only scaled by λ_i $(\vec{b} = \lambda \cdot \vec{a})$.

The λ_i and $\vec{a}_i$ which fulfill these conditions are called the
Eigenvalues and **Eigenvectors** (Heisenberg speak) or **Eigenfunctions** (Schrödinger speak) of $\overline{M}$
(*Don't worry if you do not fully understand this equivalence between vector and function.
However, see the pdf file about this question on the web site*)

You can find in mathematics books (algebra) many theorems where properties of $\overline{M}$ are linked with properties of the $\vec{a}_i$ and λ_i.
(eg *if $\overline{M}$ is such and such, then all $\vec{a}_i$ will be different, or the same, or positive or ...*)
You have probably studied this in algebra in your undergraduate curriculum. As stated above, they appear in many places

In our case $\overline{M}$ will contain not only numbers, but also derivatives $\frac{\partial ...}{\partial ....}$ and will be called the Hamiltonian, or Hamilton Operator $\hat{H}$, the vectors $\vec{a}_i$ will become the wavefunctions ψ_i and the λ_i will be the energy eigenvalues E_i.
This makes the math more complicated, but not fundamentally different

Note: matrices have properties that may seem unusual, thus

$$\overline{M}_1\,\overline{M}_2 \neq \overline{M}_2\,\overline{M}_1$$

except in special cases. Mr. Heisenberg used this property to write down his famous uncertainty principle.

This means:
If I multiply a vector $\vec{x}$ first by $\overline{M}_1$ and then by $\overline{M}_2$ $(\overline{M}_2\overline{M}_1\vec{x})$, the result will generally not be the same as multiplying first by $\overline{M}_2$ and then by $\overline{M}_1$ $(\overline{M}_1\overline{M}_2\vec{x})$

Exercise (from MIT `http://math.mit.edu/~gs/linearalgebra/ila0601.pdf`)
Show that the matrix $\begin{bmatrix} 0.8 & 0.3 \\ 0.2 & 0.7 \end{bmatrix}$ has the eigenvectors $\begin{bmatrix} 1.0 \\ -1.0 \end{bmatrix}$ and $\begin{bmatrix} 0.6 \\ 0.4 \end{bmatrix}$.
and find the associated eigenvalues λ_1 and λ_2

$$\begin{bmatrix} 0.8 & 0.3 \\ 0.2 & 0.7 \end{bmatrix} \cdot \begin{bmatrix} 1.0 \\ -1.0 \end{bmatrix} = \begin{bmatrix} 0.8 \cdot 1.0 + 0.3 \cdot -1.0 \\ 0.2 \cdot 1.0 + 0.7 \cdot -1.0 \end{bmatrix} = \begin{bmatrix} 0.5 \\ -0.5 \end{bmatrix} = \frac{1}{2} \cdot \begin{bmatrix} 1.0 \\ -1.0 \end{bmatrix}$$

so the eigenvalue is $\lambda_1 = \frac{1}{2}$
Try the other one

The link between Heisenberg's description of quantum mechanics (operators, matrices) and Schr̈dinger's (differential equations) comes from the fact that any Hamiltonian (Hamilton operator) $\hat{H}$ can be written as:

$$\hat{H} = \hat{T} + \hat{V} \qquad \hat{T} = \text{kinetic energy operator} \quad , \quad \hat{V} = \text{potential energy operator}$$

$\hat{V}$ is the normal potential energy that characterizes our problem,
eg Coulomb ($V(r) \propto \frac{1}{r}$, harmonic ($V(x) = k \cdot (x - x_0)^2$) etc
$\hat{T}$ is the kinetic energy ($\frac{m \cdot v^2}{2}$), and since v is the derivative of r (or of x or ...) $\hat{T}$ will contain derivatives, for reasons you can read about in books, second derivatives. Thus

$$\hat{H}\psi_i = \hat{T}\psi_i + \hat{V}\psi_i$$

will be a (second order differential equation for ψ, and Mr. Schrödinger (and we) will be happy

Stripped to the bones (ie all constants removed), the S.eq will thus become

$$\frac{\partial^2}{\partial x^2}\psi_i(x) + V(x) \cdot \psi_i(x) = ... = E_i \cdot \psi_i(x)$$

so we look for functions $\psi(x)$ which are, except for a factor E_i and some value $V(x)$, equal to their own second derivatives.

We know such functions, eg the cos-function, or the exp-function, and others
suitable to write our ψ functions.

With this in mind, study the basic ideas in:
– the 'particle in a box' problem
– the 'harmonic oscillator' problem
– the 'hydrogen atom' problem

You will see that only the $\hat{V}$ part of the Hamiltonian $\hat{H}$ is different
but the resulting wave functions ψ_i and eigenenergies E_i are completely different
see also table in lecture notes

For each system there is an equation that gives these energies E_i as a function of
the parameters in $\hat{V}$ and the mass m, which is in $\hat{T}$
The counting (quantum) numbers, generally called i above, have, mostly for historic reasons, different names, eg $n, v, ...$, for the different problems. Sometimes the counting starts at 0, sometimes at 1.

Note that there is always a lowest energy, called the ground state energy
This energy is **never zero**

This is related to Heisenberg's uncertainty principle, which is something unique to quantum behavior, and which states that certain properties, eg the position x and the momentum $p = mv$, cannot be determined simultaneously with arbitrary precision

If I measure a position $x \pm \Delta x$ with a small uncertainty Δx, then if I measure
at the same time $p \pm \Delta p$, Δp will be large, and vice-versa

$$\Delta x \cdot \Delta p \geq \frac{\hbar}{2}$$

Apply this to the 'particle in the box'

If the particle is 'in the box', ie $\psi(x) = 0$ outside of the box, then we know (have measured) the position of the particle (in the box) within $\Delta x \propto$ box size.
Thus we will 'automatically' have $\Delta p > 0$, which means p cannot be equal 0, and so p^2 cannot be zero, and so the kinetic energy T cannot be zero, $\Rightarrow$ the Zero Point Energy ZPE

Check
The larger the box L, the larger Δx, the smaller Δp (Heisenberg), the smaller ZPE

The same argument works, mutatis mutandis, for the harmonic oscillator

Connection with last week's homework: molecules

Writing $\hat{H}$ for the N electrons in a molecule is easy when we keep the positions of the nuclei fixed (somewhere, not necessarily at the equilibrium positions, which we do not know anyhow)

$$\hat{H} = \sum_i^N \hat{T}^{\text{electron}} \ + \ \hat{V}^{\text{electron}-\text{nuclei}} \ + \ \hat{V}^{\text{electron}-\text{electron}}$$

and each $\hat{V}$-term is a sum of many Coulomb energies $\mathcal{C}\frac{q_i q_j}{r_{ij}}$
The S-eq with this Hamiltonian cannot be solved exactly, and many approximations have been proposed to do this ($\rightarrow$ quantum chemistry). We shall not discuss this point.

In any case, we will get (approximate) energies E_i and approximate wave functions ψ_i
(except for DFT, where we get ψ^2 instead of ψ, which is a loss of information (phase, interference, no quantum computing with DFT!)
DFT also needs more approximations, the famous 'functional' you may have heard about in Aj.Montree's class)

Depending on the approximation used, the computer, and computer time (hours, days, weeks), available, one can treat systems (single molecules or groups of molecules) with up to 1000-3000 electrons.
(*This is not very much if you think about a condensed phase with* $\approx 10^{20}$ *molecules*)

Results
– Often we need only the lowest energy, the ground state
– However, for (electronic) spectroscopies we need also excited states
– We can use ψ to compute molecular properties (dipole, NMR, ...)
  sometimes ψ^2 is enough
– We can explore how the ground state energy depends on the (assumed) positions of the nuclei
  and try to find the geometry with the lowest electronic ground state energy ($\rightarrow$ PES)
– Many things can then be computed from the PES (vibrations, statistical mechanics)
– We can make plots to visualize the geometry, ψ, and ψ^2

For us in CHE502 and CHE501, the PES will be the most important 'output'