Approximate Methods

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Outline of the lecture I

We are going to be dealing with many-body (i.e., many electron) wavefunctions. So we will begin by looking at what we know about these wavefunctions and what tools we have to analyse them:

- Properties of Ψ: All the exact properties the wavefunction (and density) are expected to satisfy. Afterall, any approximate wavefunction should satisfy as many of these as is practically possible.
- Methods for approximating the wavefunction. We cannot solve much beyond the 1-electron, hydrogen atom. For anything more complex, we must solve the Schrödinger equation approximately.
- Mathematical methods: We will need some advanced mathematical methods in this course.

Approximate Methods I

What are the methods available to solve the Schrödinger equation for many electron systems?

- Variational principle
- Perturbation theory
- Non-perturbative, approximate methods
- Stochastic methods

Before moving on to the many-body problem, we will re-visit the first two methods in a fairly basic way. You have already seen these before, but let's go over these again. The non-perturbative methods will be covered later in the course. Stochastic methods form a special topic and should be the subject of another course, but we may be able to discuss them at the end, should we have time. We won't!

The Variational Method I

We will follow Sec. 1.3 in Szabo & Ostlund.

Our goal is solve the eigenvalue problem:

$$\mathcal{H}|\Psi\rangle = \mathcal{E}|\Psi\rangle,$$

where $|\Psi\rangle$ is the exact (usually g.s.) wavefunction with energy eigenvalue $\mathcal{E}$.
Assume that we know the complete set of orthonormal solutions to $\mathcal{H}$. This is normally an uncountable set, but here, for simplicity we will index these solutions

$$\mathcal{H}|\Psi_\alpha\rangle = \mathcal{E}_\alpha|\Psi_\alpha\rangle, \qquad \alpha = 0, 1, \cdots$$

The Variational Method II

and assume that we have ordered the eigenvalues s.t.

$$\mathcal{E}_0 \leq \mathcal{E}_1 \leq \mathcal{E}_2 \leq \cdots$$

The solutions are orthonornal, so

$$\langle \Psi_\alpha | \Psi_\beta \rangle = \delta_{\alpha\beta}.$$

Any trial wavefunction can be written in terms of this complete set:

$$|\tilde{\Psi}\rangle = \sum_\alpha |\Psi_\alpha\rangle c_\alpha = \sum_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha|\tilde{\Psi}\rangle$$

and, similarly, for the c.c.

$$\langle\tilde{\Psi}| = \sum_\alpha c_\alpha^* \langle\Psi_\alpha| = \sum_\alpha \langle\tilde{\Psi}|\Psi_\alpha\rangle\langle\Psi_\alpha|$$

The Variational Method III

We will now prove the Variational Principle in its usual form that states that if

$$\langle\tilde{\Psi}|\tilde{\Psi}\rangle = 1$$

then

$$\langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle \geq \mathcal{E}_0.$$

Q: First show that

$$\langle\tilde{\Psi}|\tilde{\Psi}\rangle = 1 = \sum_\alpha |\langle\Psi_\alpha|\tilde{\Psi}\rangle|^2$$

The Variational Method IV

Now consider

$$
\begin{aligned}
\langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle &= \sum_{\alpha\beta}\langle\tilde{\Psi}|\Psi_\alpha\rangle\langle\Psi_\alpha|\mathcal{H}|\Psi_\beta\rangle\langle\Psi_\beta|\tilde{\Psi}\rangle \\
&= \sum_{\alpha}\mathcal{E}_\alpha|\langle\Psi_\alpha|\tilde{\Psi}\rangle|^2 \\
&\geq \sum_{\alpha}\mathcal{E}_0|\langle\Psi_\alpha|\tilde{\Psi}\rangle|^2 = \mathcal{E}_0\sum_{\alpha}|\langle\Psi_\alpha|\tilde{\Psi}\rangle|^2 = \mathcal{E}_0
\end{aligned}
$$

Q: Solve Exercise 1.19 from S & O

The Variational Method V

We will make extensive use of trial wavefunctions expanded in a linear combination of fixed basis functions.

To save space we will use a different notation: The trial function will be $|\tilde{\Psi}\rangle = |\mathbf{c}\rangle$ and the basis functions will be $|i\rangle$.

$$|\tilde{\Psi}\rangle = |\mathbf{c}\rangle = \sum_{i=1}^{N} c_i |i\rangle$$

We will not assume that the basis functions are orthogonal (S & O assume they are), that is

$$\langle i|j\rangle = S_{ij} = (\mathbf{S})_{ij}$$

where **S** is called the overlap matrix.

The Variational Method VI

We also define the Hamiltonian matrix:

$$(\mathbf{H})_{ij} = H_{ij} = \langle i|\mathcal{H}|j\rangle.$$

In this notation,

$$\langle\tilde{\Psi}|\tilde{\Psi}\rangle = \langle\mathbf{c}|\mathbf{c}\rangle = \sum_{ij} c_i^* c_j \langle i|j\rangle = \sum_{ij} c_i^* S_{ij} c_j$$

Similarly, show that

$$\langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle = \langle\mathbf{c}|\mathcal{H}|\mathbf{c}\rangle = \sum_{ij} c_i^* H_{ij} c_j$$

We need to minimize $\langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle$ s.t. $\langle\tilde{\Psi}|\tilde{\Psi}\rangle = 1$. To do the former and enforce the latter we use the method of Lagrange multipliers (see Mathematical Methods for Physicists by Arfken, Weber and

The Variational Method VII

Harris) and impose the normalisation requirement using a constraint. Define the function

$$\mathcal{L}(E, c_1, c_2, \cdots) = \langle\tilde{\Psi}|\mathcal{H}|\tilde{\Psi}\rangle - E(\langle\tilde{\Psi}|\tilde{\Psi}\rangle - 1),$$

where E is the Lagrange multiplier. We have chosen to use the letter ‘E’ with a negative sign as we will see that this multiplier will end up being the energy. The minimum (actually, extremum) is achieved when

$$\frac{\partial\mathcal{L}}{\partial c_k^*} = 0 = \frac{\partial\mathcal{L}}{\partial c_k}.$$

We will use the first condition:

$$0 = \frac{\partial\mathcal{L}}{\partial c_k^*} = \sum_j c_j H_{kj} - E\sum_j c_j S_{kj},$$

The Variational Method VIII

or, changing dummy variables,

$$\sum_j H_{ij} c_j - E \sum_j S_{ij} c_j$$

or, in matrix form

$$\mathbf{H}\mathbf{c} - E\mathbf{S}\mathbf{c} = 0$$
$$(\mathbf{H} - E\mathbf{S})\mathbf{c} = 0$$

For these set of linear equations to have non-trivial (i.e., non-zero) solutions, we must have

$$\boxed{\det(\mathbf{H} - E\mathbf{S}) = |\mathbf{H} - E\mathbf{S}| = 0.}$$

The Variational Method IX

This gives us N solutions which we will order as

$$E_0 \leq E_1 \leq E_2 \leq \cdots E_N.$$

For each energy, E_α, we have a solution vector of coefficients $\mathbf{c}_\alpha$, s.t.

$$(\mathbf{H} - E_\alpha \mathbf{S})\mathbf{c}_\alpha = 0.$$

Or,

$$\mathbf{H}\mathbf{c}_\alpha = E_\alpha \mathbf{S}\mathbf{c}_\alpha.$$

The eigenfunctions can be calculated as:

$$|\tilde{\Psi}_\alpha\rangle = |\mathbf{c}_\alpha\rangle = \sum_i C_{i\alpha}|i\rangle,$$

The Variational Method X

where the matrix element $C_{i\alpha} = (\mathbf{c}_\alpha)_i = (\mathbf{C})_{i\alpha}$. We will henceforth treat $\mathbf{C}$ as a matrix, and, if we are interested in a particular column vector we will use the notation $\mathbf{c}_\alpha$.

Now, if we use an orthonormal basis, then $\mathbf{S} = \mathbf{I}$, giving

$$\mathbf{H}\mathbf{c}_\alpha = E_\alpha \mathbf{c}_\alpha,$$

which now looks like a standard eigenfunction equation, only here the eigenfunction is a vector from which the function can be calculated as shown above.

The Variational Method XI

The eigenfunctions $|\tilde{\Psi}_\alpha\rangle$ can be made orthonormal (see S & O, Sec. 1.1.6), so $\langle\tilde{\Psi}_\alpha|\tilde{\Psi}_\beta\rangle = 1$. Show that, when $\mathbf{S} = \mathbf{I}$, this implies that

$$\mathbf{C}^\dagger \mathbf{C} = \mathbf{I}.$$

Q: I.e., the matrix **C** is unitary. Also show that

$$\mathbf{C}^\dagger \mathbf{H} \mathbf{C} = \mathbf{E},$$

where the energy matrix is a diagonal matrix defined as $E_{\alpha\beta} = E_\alpha \delta_{\alpha\beta}$. This shows us that the solution **C** is the matrix that diagonalises the Hamiltonian matrix **H**.

The Variational Method XII

Q: Solve questions 1.21 and 1.22 in Szabo & Ostlund. The first will show you how the variational principle can be extended to excited states, and the second is an application of this principle to calculate the polarizability of the hydrogen atom.

The Variational Method XIII

The (linear) Variational principle is deceptively simple and tremendously useful. All of Hartree–Fock theory, configuration interaction, and density functional theory are based on this principle.
We will come back to this shortly, but let us look ahead a bit:

- We expanded our wavefunction in a linear combination of basis functions and then used the variational principle to find the best coefficients.
- How do we choose the basis functions?
- A convenient choice will be to use atomic-like functions as the basis functions.

The Variational Method XIV

- These atomic orbitals will include ground and excited states of the atoms. After all, when bonds are formed, the atoms are not in their ground states: they will be in some linear combination of ground and excited states.
- So the molecular wavefunction is expanded as a *linear combination of atomic orbitals*. This, LCAO, model is used in most electronic structure calculations.
- The success of this approach depends on the completeness of the basis set. It turns out that we cannot really use true atomic orbitals as we cannot even solve the helium atom to get all of these. In any case, even if we did have the atomic states, how could we possibly include enough of them?

The Variational Method XV

- In any case, the true many-body wavefunction is not easy to write down. We always approximate it in some way, and then expand the appoximation in a linear combintation of basis functions.
- This means that our variational solution will be approximate. And we therefore need to find ways of correcting it.
- One such way is perturbation theory.

Raleigh–Schrödinger Perturbation Theory I

We will now briefly recap of Raleigh–Schrödinger perturbation theory. We use perturbation theory when we cannot solve a differential (or any other) equation exactly, but can find solutions to the major part of it; we then treat the remainder as a perturbation over the solution we can find. This is how it works:

- Split the Hamiltonian into two parts:

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{V}$$

  where $\mathcal{H}_0$ is a Hamiltonian which we know how to solve and $\mathcal{V}$ contains that troublesome parts. We expect $\mathcal{V}$ to be a perturbation so it must be small in some sense.

Raleigh–Schrödinger Perturbation Theory II

- λ is a complex number that will be 1 for the physical solution. We start with $\lambda = 0$: This gives the solution we already know. Then we consider small, but non-zero λ; develop a perturbation expansion; and take the limit $\lambda \to 1$, with the hope that the expansion is still meaningful (or convergent) in this limit. Physicists hope; Mathematicians know!
- Let the solutions of $\mathcal{H}_0$ be:

$$\mathcal{H}_0 \Psi_i^{(0)} = E_i^{(0)} \Psi_i^{(0)}$$

Here the '0' indicates that these eigenvalues and eigenfunctions are of *zeroth*-order in the perturbation $\mathcal{V}$. We will use the short-form:

$$|\Psi_i^{(0)}\rangle \equiv |i\rangle$$

Raleigh–Schrödinger Perturbation Theory III

- Express the solutions of $\mathcal{H}$ in a power-series:

$$\Psi_i = \Psi_i^{(0)} + \lambda \Psi_i^{(1)} + \lambda^2 \Psi_i^{(2)} + \cdots = \sum_n \lambda^n \Psi_i^{(n)}$$

$$E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots = \sum_n \lambda^n E_i^{(n)}$$

- Intermediate normalization: $\langle i | \Psi_i \rangle = 1$.

$$\begin{aligned} 1 =& \langle i | \Psi_i \rangle \\ =& \langle i | i \rangle + \sum_{n=1}^{\infty} \lambda^n \langle i | \Psi_i^{(n)} \rangle \end{aligned}$$

Raleigh–Schrödinger Perturbation Theory IV

Since $\langle i|i\rangle = 1$, and since this result must hold for all λ, therefore we equate powers of λ to show that

$$\langle i|\Psi_i^{(n)}\rangle = 0 \quad \forall n \geq 1.$$

- Substitute the expansions into the Schrödinger equation and equate powers of λ. We get

$$\begin{aligned}
\lambda^0 &: \quad \mathcal{H}_0|i\rangle = E_i^{(0)}|i\rangle \\
\lambda^1 &: \quad \mathcal{V}|i\rangle + \mathcal{H}_0\Psi_i^{(1)} = E_i^{(1)}|i\rangle + E_i^{(0)}\Psi_i^{(1)} \\
\lambda^2 &: \quad \mathcal{H}_0\Psi_i^{(2)} + \mathcal{V}\Psi_i^{(1)} = E_i^{(2)}|i\rangle + E_i^{(1)}\Psi_i^{(1)} + E_i^{(0)}\Psi_i^{(2)}
\end{aligned}$$

Raleigh–Schrödinger Perturbation Theory V

- Take the inner product with $\langle i|$ to get simple expressions for the energies at various orders:

$$\begin{aligned} E_i^{(0)} &= \langle \Psi_i^{(0)}|\mathcal{H}_0|\Psi_i^{(0)}\rangle = \langle i|\mathcal{H}_0|i\rangle \\ E_i^{(1)} &= \langle \Psi_i^{(0)}|\mathcal{V}|\Psi_i^{(0)}\rangle = \langle i|\mathcal{V}|i\rangle \\ E_i^{(2)} &= \langle \Psi_i^{(0)}|\mathcal{V}|\Psi_i^{(1)}\rangle \end{aligned}$$

- To find the second-order energy correction we need the first-order correction to the wavefunction. Expand this correction in the basis of eigenstates of the unperturbed Hamiltonian $\mathcal{H}_0$ with coeffs $c_n^{(1)}$:

$$\Psi_i^{(1)} = \sum_n c_n^{(1)}|n\rangle.$$

Raleigh–Schrödinger Perturbation Theory VI

- Since $\langle i|\Psi_i^{(n)}\rangle = 0$ (see above), it follows that $c_i^{(1)} = 0$. Hence the state $|i\rangle$ does not contribute to the expansion. We indicate this with a *prime* in the summation:

$$|\Psi_i^{(1)}\rangle = \sum_n{}' c_n^{(1)}|n\rangle.$$

- Insert this expansion in the (re-arranged) λ^1 differential equation:

$$(E_i^{(0)} - \mathcal{H}_0)|\Psi_i^{(1)}\rangle = (\mathcal{V} - E_i^{(1)})|i\rangle$$

And taking the inner product with $\langle m|$, show that

$$c_m^{(1)} = \frac{\langle m|\mathcal{V}|i\rangle}{E_i^{(0)} - E_m^{(0)}}.$$

Raleigh–Schrödinger Perturbation Theory VII

- Hence the first-order correction to the wavefunction is given by

$$|\Psi_i^{(1)}\rangle = {\sum_n}' \frac{|n\rangle\langle n|\mathcal{V}|i\rangle}{E_i^{(0)} - E_n^{(0)}}$$

- So we get for the second-order energy correction:

$$E_i^{(2)} = {\sum_n}' \frac{|\langle n|\mathcal{V}|i\rangle|^2}{E_i^{(0)} - E_n^{(0)}}$$

Higher-order corrections to the wavefunction and the energy can be obtained by keeping more and more terms in the expansion. We often use these, but we must not assume that they will be meaningful. The problem here is that we cannot guarantee the convergence of perturbation expansions. These expansions are often divergent (bad!) or only asymptotically convergent (use with care!).

Raleigh–Schrödinger Perturbation Theory VIII

Q: Fill in the steps in the above proof for the second-order energy correction. State any assumptions that may have been made. You will find a full proof in Ch. 6 of the book by Szabo & Ostlund.

Q: When do you expect perturbation theory to fail?

Raleigh–Schrödinger Perturbation Theory IX

Question (PT 1): Polarizability of the hydrogen atom
For an atom (spherically symmetrical) placed in an electric field F (we will use F so as not to confuse the field with the energy), the polarizability α appears at second-order in the energy when it is expanded in terms of the field, that is,

$$E(F) = E(0) - \frac{1}{2}\alpha F^2 - \mathcal{O}(F^4).$$

The polarizability is a tensor (matrix), but for a spherically symmetrical system it is diagonal with all elements equal so we may treat it as a number.
We will now use RSPT to evaluate the polarizability of the hydrogen atom in its g.s. The Hamiltonian for this system is

$$\mathcal{H}_0 = -\frac{1}{2}\nabla^2 - 1/r,$$

Raleigh–Schrödinger Perturbation Theory X

with g.s. wavefunction $\Psi_0^{(0)} = e^{-r}/\sqrt{\pi}$, and g.s. energy $E_0^{(0)}$. The electric field F creates a perturbing potential $\mathcal{V} = Fz$. We have used a field along z.

Show that $E_0^{(1)} = 0$. Why would you expect it to vanish? Use this result to show that the first-order wavefunction satisfies the differential equation

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{1}{2}\right)\Psi_0^{(1)} + \frac{1}{\sqrt{\pi}}Fze^{-r} = 0,$$

and verify that

$$\Psi_0^{(1)} = -\frac{1}{\sqrt{\pi}}\left(1 + \frac{r}{2}\right)Fze^{-r}$$

is a solution.

Raleigh–Schrödinger Perturbation Theory XI

Hence find the second-order energy $E_0^{(2)}$ and deduce the polarizability of the hydrogen atom.
Now use the sum-over-states expression for $E_0^{(2)}$ to solve this problem. You may limit the sum to the *p*-orbitals of hydrogen.
How does this result compare with the previous one?