Q&A Lecture 6

Do we get a particular advantage deriving the SE this way in a coordinate basis? I don't necessarily understand the reason or goal to do this.

The practical advantage might be showing that we can turn the search for the solution of a partial differential equation (i.e. the standard expression of the time independent Sch. equation, TIS) into an optimization problem that identifies the minimum of the variational problem. Numerically, there are pros and cons to both approaches so being able to adopt one or the other, depending for example on the specific system under study, can be useful. There is also a conceptual advantage - in my view important - in that this way of deriving the TIS shows another analogy with classical mechanics since also for classical systems one can derive the evolution equations by minimizing a functional (in that case, the action functional). Furthermore, this shows that quantum mechanics is a variational theory…and so provides a different overall view and paths to understanding of the theory.

If the time-independent Schrodinger equation solution wave function gives, after normalization, the trial state with the ground level energy, what is the point of guessing a trial wavefunction yourself?

The variational principle needs a trial wavefunction as an input and outputs an OPTIMISED state, in the sense that it is the state with a form compatible with that of the trial wavefunction that minimises the Rayleigh ratio. You have seen this in the TA with Edrick in which he "guessed" a Gaussian form with an undetermined parameter, the variance, and then used the variational principle to get an equation to determine that parameter…and from the state with the FIXED parameter the estimate of the ground state energy. Similarly, if we say that the trial state is given by a linear combination (with UNKNOWN coefficients) of a finite size basis set, we input that in the variational principle and obtain equations for the coefficients. The obtained coefficients determine the actual the state.

If the trial function is continuous as well as the basis, how can we derive for all the phi(x) to get the best estimator?

Not sure I understand: if you mean formally, then the answer is that the math of functionals enables us to do so as shown in class. If you mean in an algorithm for a computer, then the answer is that we (as always) discretize, either by directly introducing a grid or by discretizing a basis set (e.g. plane waves). We'll see more about this in future lectures.

I have understood that if the temperature is constant, we generally use a thermostat and methods to extract the targeted subsystem from the system. I have not really understood what are the two families of thermostats. Could you explain me that, please?

Deterministic (à la Nose-Hoover) and stochastic (à la Langevin) thermostats. In both cases, the Hamiltonian evolution equations (that sample a NVE ensemble) are modified to define an evolution equation that generates a trajectory that sample the NVT ensemble. This is done by trying to reduce as much as possible the additional numerical effort. We'll discuss both techcniques in more detail in the next class.

I did not really understand why we decided to take the functional derivative when the equation had the shape E<p|p> = <p|H|p> instead than when we have E = <p|H|p>/<p|p> besides that it lead to time independent Schrodinger equations, what was the purpose of this and how does it help us find the ground state energy ?

The rewriting was done precisely to get to the time-independent Sc. equation. In doing so, we can show that this equation is variational which has important theoretical implications (and it provides yet another view with a classical analog). In practice, this derivation does not lead to more EXACT solution methods — it can obviously be used in the context of the variational approach as we have done before the rewriting.

In the lecture, the idea of constraints in tandem with minimising energy was introduced. Would applying a constraint(s) allow us to increase the timestep used in an algorithm? But on the other hand, would doing this reduce the accuracy of calculations?

In a different context. Constraints were originally introduced in MD to block fast motions such as fast vibrations around the equilibrium distance value in the distance between atoms in a diatomic molecule and focus on translational and rotational motions (typically slower) for the system. In this case, the use of constraints does enable use of a larger time step.

Not really: it is a change in the model of the system, but the biasing effect of the constraint on the average properties of degrees of freedom that are left (translational and rotational in the example above) can be corrected exactly to lead to the unbiased values.

I have a technical problem when deriving the Schrodinger equation from the Variational principle. If we don't assume the wave function is real, what does the

derivative of \delta(\psi^*(x)) with respect to function $\psi(x')$ equal to, i.e., $\delta(\psi^*(x))/ delta(\psi(x')) = ?$ Is it still the delta function $\delta(x - x')$?Is it necessary to have this assumption?

In this case, we treat the wavefunction and its complex conjugate as two independent "variables" and take the derivative with respect to either of them (typically the complex conjugate of \psi). The choice is not critical because the equations obtained via derivation with respect to one is the complex conjugate of the other; Yes; What assumption: orthonormality is necessary, a real wavefunction is not (see above).

As we get the exact Schröedinger equation out of the functional equation, when we do the variational principle by optimising with the functional, can we get the exact ground energy ? If not, where the approximation comes from ?

Dumb questions are very rare and this is not one of them! The Schr. gives the equation that provides the exact solution of the variational problem. If we can solve the Schr. equation (as obtained from the variational principle or in general) exactly we get the full set of eigenvalues and eigenvectors of the Hamiltonian and, among these, the exact ground energy.

The way in which we solve in practice is by GUESSING a form for the solution and then identifying the optimal solution of THE GUESSED form via the variational principle. The approximation comes from having imposed a specific form for the solution (if we are good enough - but I, for example, am generally not — to guess the form of the exact solution we get the exact ground state energy).

How are the lagrangian multipliers related to the variational method, what kinds of contraints are involved from a physical point of view ?

The Lagrange multipliers are used in the variational method to impose the constraint of normalization of the optimised trial function. In the case of a wavefunction, the normalisation of the state represent the physical requirement that the probability to "find the system anywhere in space" must be one because the system is certainly anywhere in space.

Can we have functionals that are time-dependent? I mean, is it possible to have a functional Y[f, t], where f is a function? Or do we need to factor in the time dependence only through f, and the functional cannot explicitly depend on time?

We can have functionals that are also explicit functions of time, yes. An important example is the action functional in classical mechanics. Note that this is the functional that, upon minimisation, leads to the classical evolution equations (typically in Lagrangian form).

In the model we discussed for the constant temperature world, can particles be transferred from one system to the other with their energy?

No, particles cannot be exchanged as we are discussing the NVT (or canonical ensemble). There are methods to simulate systems that can exchange energy, these correspond to constant chemical potential systems (such as the grand-canonical ensemble).

We can realize the time-independent Schrödinger equation from the variational principle, and hence the optimized energy corresponds to a time-independent quantum problem. How do we realize the variational principle for a quantum system that evolves in time?

There is a generalization of the approach that starts from the definition of an "action" and minimises that to obtain evolution equations - and not eigenfunction equations like we have seen in class.

We want to find a wave function that minimizes the energy such as its normalization constant equals 1, but why is it important ? Doesn't the Rayleigh ratio account for non-normalized wave functions with its denominator ?

The normalisation is important for the physical interpretation of the square of the wavefunction (for example) as a probability (density). In the coordinate representation, the normalisation equal to one means that the probability to find the system anywhere in space is one. The presence of the norm at the denominator of the ratio may "renormalise" the ratio but it is not sufficient to provide normalised states.

I have a follow up question : since the system behaviour and description is well defined for a given simulation problem (let's say we know which interaction are relevant). As the variational principle depends on the Hamiltonian, if we have 2 systems that evolve under the same assumption but with different parameters (particle's mass / number of particles / boundaries / etc..), will the optimal function's form to minimise the variational principle for each instance be the same (up to some parameters involved) or they will lead to different optimal function's form? If they are the same, do we know what are the optimal function form for some problems (for example simples ones like harmonic oscillators) ?

If the optimal solution is the "best possible" solution, it coincides with the exact solution of the Schrödinger equation for the system. In this case, if we can determine it, it will have a general - same form - when we chage parameters, as you say minus the dependence on these parameters.

Yes we do, you can find a collection of problems for we we know the exact ground state in Shankar.

I think that the argument on parametric dependence can be carried through even if we are looking at the "best solution" given a trial wave function that is not the exact ground state. As for the second part of the question, there are some consolidated variational functions that are used, for example, for molecular systems — so we know forms that are ok even if not exact.