Overview of QM IV

Finding Ground States

Even today, finding ground state energies and configurations occupies an inordinate portion of the theoretical physics effort.

1 Perturbation theory is bedrock for many-body problems

\[
E = E_o + \sum_{m>o} \frac{|\langle m | H | 0 \rangle|^2}{E_o - E_M} < E_o!
\]

Questions: Does it converge? If not, what then?
What if \( |0 \rangle \) is orthogonal to ground state?

2 Variational theory is complement to perturbation theory

Variational state must be orthogonal to ground state and must contain terms with the same symmetry.

Configuration Interaction theory uses a finite set of basis states to construct variational wavefunction with one to four excitations from the Hartree-Fock “starter” ground state: single, double, triplet, quadruple. The number of configurations grows exponentially with the number of electrons, limiting the size of system computable.

Quantum Monte Carlo statistically computes, by importance sampling, the ground state energy with an algorithm that iteratively the wave function. Its acceptance is slowing growing.

3 Approximate methods

Other theoretical work on ground states uses approximate methods: devising model Hamiltonians that might be exactly soluble. History suggests that either the models are insoluble or they poorly mimic real problem. All face the same problem: If the results don’t agree with experiment, is the source the model Hamiltonian or the approximation?

Beyond the ground state

While knowing the ground state is important, it is usually a poor guide to excited states and properties of the problem. Example: given a good ground state for an atom, how well could you compute the excited states and magnitude of single- and multi-photon absorption. including processes occurring above the ionization energy?

There are no systematic methods for improving excited states.

To date there is no sustained effort in CI or equivalent methods for finding accurate excited states. The workhorse of condensed systems, density functional theory, after two decades of improving its central approach – the exchange-correlation energy – has limited successes with computing excited states,

4 Approximate methods

Most methods use the excited states found by the approximate Hamiltonian: e.g., Hartree-Fock, Density-Functional. While there is limited successes in computing spectral positions and intensities, all improvements are ad hoc.
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5 Transport Theory and Dynamics

Most technology depends either on the mechanical or electrical (especially transport) properties of materials. Neither is on firm theoretical foundation. Fortunately empirical experience has served technology well.

In the future, as increasingly smaller systems are used – nanotechnology – theory must take a larger role in refining the systems before empirical testing. This role involves not only predicting a small range of likely materials but also their initial performance and subsequent degradation with use. The dominance of theory lies in the future.