Introduction to computational quantum mechanics

Lecture 4: Common quantum systems

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Brief summary of last lecture

The Hamiltonian

Pedestrian overview of common quantum systems

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Summary 1

We summarize the key points from the last lecture:

▶ One-particle Hilbert space:

\[ \mathcal{H}_1 = L^2(\mathbb{X}) = \text{Span}\{ \phi_n \}_{n=1}^{\infty}; \quad \mathbb{X} = \text{config. space} \]

▶ N-fermion Hilbert space:

\[ \mathcal{H}_N = \Pi_- \mathcal{H}_1^N = \text{antisymmetric functions of } N \text{ coordinates} \]

▶ Basis functions for \( \mathcal{H}_N \):

\[ \Phi_{n_1, \ldots, n_N}^{SD} = c_{n_1}^{\dagger} \cdots c_{n_N}^{\dagger} \Phi_0^{SD} \]

where

\[ c_{n}^{\dagger} = \text{creation operator for one-particle basis function ("orbital") } \phi_n \]
In $\Phi_{\vec{n}}^{SD}$ we only consider $\vec{n}$ such that

$$n_1 < n_2 < \cdots n_N,$$

i.e.,

$$\vec{n} \longleftrightarrow \alpha = \text{subset of } \mathbb{N} \text{ with } N \text{ elems} \quad \Rightarrow \quad \text{binary integer with } N \text{ set bits}$$

Fock space:

$$\tilde{\mathcal{H}} := \bigoplus_{N=0}^{\infty} \mathcal{H}_N.$$

Notice that this is a Hilbert space whose elements are functions of a varying number of coordinates $x_k \in X.$
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The $N$-particle Hamiltonian

A very general Hamiltonian for an $N$-particle system is:

$$H : \text{D}(H) \subset \mathcal{H}_N \to \mathcal{H}_N$$

$$H = \sum_{k=1}^{N} H_0(k) + \sum_{k=1}^{N-1} \sum_{j=k+1}^{N} V(k,j)$$

Here, $H_0 : \text{D}(H_0) \subset \mathcal{H}_1 \to \mathcal{H}_1$ and $V : \text{D}(V) \subset \mathcal{H}_2 \to \mathcal{H}_2$. We say that “$H_0$ is a one-particle operator, and $V$ is a two-particle operator.” Moreover,

- $H(k) :$ acts only on coordinate $x_k$
- $V(j,k) :$ acts only on coordinates $x_j$ and $x_k$

Note the sum over all particles in the first term, and all pairs in the second.
Example

- Hilbert space:
  \[ \mathcal{H}_1 = L^2(\mathbb{R}), \quad \mathcal{H}_N = \Pi_\mathcal{H}_1^N \subset L^2(\mathbb{R}^N) \]

- Kinetic energy operator \( H_0 = T \) on this space:
  \[ T : D(T) \to \mathcal{H}_1, \quad T = -\frac{\hbar^2}{2m} \nabla^2. \]

- Kinetic energy for particle \( k \):
  \[ T(k) = -\frac{\hbar^2}{2m} \nabla_k^2. \]

- Note: \( \sum_k T(k) = -\frac{\hbar^2}{2m} \Delta \)

- Two-particle interaction:
  \[ V : D(V) \subset \mathcal{H}_1^2 \to \mathcal{H}_1^2, \quad V = u(\|x_1 - x_2\|) \]
Classical analog of example

Figure: A collection of $N$ particles, with no discrete degrees of freedom, living on $\mathbb{R}^2$. Each particle $x_j$ feels a force $v(\|x_j - x_k\|)$ from every other particle $x_k$. 
Properties of $H$

- We assume that $H^* = H$, and that $H \geq b$, i.e., it is bounded from below:

$$\sigma(H) \subset [b, +\infty)$$

This is true for a wide class of Hamiltonians, and depends only on $V$ in our example. It is not our concern.

- We assume that

$$\Phi_{\alpha}^{SD} \in D(H).$$
Matrices of self-adjoint operators

Now, we note that:

- $H$ is self-adjoint, i.e., $H^* = H$.
- The Slater determinants $\mathcal{B}_N$ are dense in $D(H)$.

It turns out, that in such cases:

$H$ may be identified with its matrix wrt the SD basis

That is, $H$ is entirely given by its action on a basis contained in $D(H)$. See Weidmann (1976) for details.
Hamiltonian in “second quantization”

It is a very useful result, that $H$ now can be written as:

$$H = \sum_{ij} \langle \phi_i | H_0 | \phi_j \rangle c_i^\dagger c_j + \frac{1}{2} \sum_{ijkl} \langle \phi_i \otimes \phi_j | V | \phi_k \otimes \phi_\ell \rangle c_i^\dagger c_j^\dagger c_\ell c_k.$$

Key observations:

- This form is essentially the matrix form, seen by acting on a $\Phi_{\alpha}^{SD}$, which produces a linear combination of other $\Phi_{\beta}^{SD}$.
- It is independent of $N$: The same expression is valid for any $N$.
- The sums are no longer over particles, but over single particle basis functions, “orbitals”.
- Note also the index order in the interaction term.
- Note that the interaction “matrix element” $\langle \phi_i \otimes \phi_j | V | \phi_k \otimes \phi_\ell \rangle$ is computed in $\mathcal{H}_1^2$, not $\mathcal{H}_2$. 
Example: single-particle operator

- Again, \( \mathcal{H}_1 = L^2(\Box) \).
- We let the single-particle basis (“orbitals”) be given by:

\[
\phi_{n,m}(x) = 2 \sin(n\pi x) \sin(m\pi y), \quad n, m = 1, 2, \ldots
\]

- Letting \( H_0 = T = -\frac{\hbar^2}{2\mu} \nabla^2 \), we obtain:

\[
\langle \phi_{n,m} | T \phi_{n',m'} \rangle = \delta_{n,n'} \delta_{m,m'} \frac{\hbar^2 (n^2 + m^2) \pi^2}{2\mu} =: t_{n,m}^{n',m'}.
\]

- The one-particle part of \( H \) becomes:

\[
\sum_{k=1}^{N} T(k) = \sum_{n,m=1}^{\infty} \frac{\hbar^2 (n^2 + m^2) \pi^2}{2\mu} c_{n,m}^\dagger c_{n,m}.
\]
There are two sources of sparsity of $H$:

- Orthonormality of orbitals $\phi_n(x)$: Similar to compact support of FEM basis functions. In the example, $t_{n,m}^{n',m'}$ was diagonal.
- The so-called Slater-Condon rules which implies: Whenever $\#(\alpha \cap \beta) < N - 2$,
\[ \langle \Phi^{SD}_\alpha | H | \Phi^{SD}_\beta \rangle = 0. \]
- Easy to see: The expression $c_i^\dagger c_j^\dagger c_\ell c_k$ removes bits $\ell$ and $k$ from $\beta$, and inserts $i$ and $j$. The result must be equal to $\alpha$ for a nonzero result! Thus, $\alpha$ and $\beta$ cannot differ in more than 2 bits.
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Atoms are the prime examples of quantum systems. Atoms are composed of

- A nucleus: $Z$ protons and $N$ neutrons. The protons are positively charged, while the neutrons are (surprise!) neutral.

- Electrons: $N_e$ of them; $N_e = Z$ for a neutral atom; a non-neutral atom is called an ion. Each electron is a spin-$\frac{1}{2}$-particle, meaning that it has a 2-valued discrete degree of freedom; values $\uparrow$ and $\downarrow$. Electrons are – as far as we know – point particles.
Figure: A hydrogen atom (left), helium-4 (right), and oxygen-16 (middle) are run-of-the-mill atoms, quite common on Earth. The drawing is not to scale! Also, the nucleons are much heavier than the electrons, which leads to the Born-Oppenheimer approximation (see later).
Scale of the hydrogen atom

**Figure:** A pea-sized proton in the middle of Ullevål, and a dust-mote-sized electron around the perimeter. The rest is vacuum!
As the nucleus is much heavier than the electrons, its motion can for the most part be ignored. Also, the size of the nucleus is much smaller than the typical length scale of the motion of the electrons:

- The nucleus is a fixed point in space with charge $Ze$, where $-e$ is the electron charge. Coulomb force: $-Ze^2/r$. 
Hilbert space and Hamiltonian for atoms

With all this in mind:

- One-particle Hilbert space: $L^2(\mathbb{R}^3 \times \{\uparrow, \downarrow\}) = L^2(\mathbb{R}^3)^2$.
- $N$ is the number of electrons, and $Z$ is the number of protons.
- Each electron feels an attractive Coulomb force from the nucleus at $\vec{r} = 0$, so the one-particle operator becomes:

$$H_0(k) = -\frac{\hbar^2}{2\mu} \nabla_k^2 - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_k\|}.$$

- The Coulomb repulsion between two electrons is

$$V(j, k) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{\|\vec{r}_j - \vec{r}_k\|}.$$

- Remarkably, in spite of the singularities, the resulting Hamiltonian is self-adjoint and bounded from below! Moreover, the EVP for $H_0$ is analytically solvable.
Nuclei

The nucleus in itself is a quantum system, whose non-relativistic approximation is as follows:

- The $A = Z + N$ nucleons are considered identical spin-$\frac{1}{2}$ particles with an additional 2-valued isospin degree of freedom.
- The value for the isospin (say, + or −) tells whether we have a proton or neutron, resp.
- One-particle Hilbert space:

$$L^2(\mathbb{R}^3 \times \{\uparrow, \downarrow\} \times \{+,-\}) = L^2(\mathbb{R}^3)^4.$$ 

- Hamiltonian:

$$H = \sum_{k=1}^{A} T(k) + \sum_{j<k}^{N} V(j,k),$$

where the interaction is basically unknown and, unlike for the atomic systems, the interaction depends on spin and isospin! This is easy to see: protons repel each other with Coulomb forces, but neutrons to not.
Nuclear systems are hard to tackle because of these reasons:

- It is **self-bound**; no natural centre around which the nucleons evolve. Consequence: purely continuous spectrum of $H$ with embedded eigenvalues.

- The interaction is **extremely strong**, but there is no known, closed form expression for it. Only experimental data and phenomenological models. (There is QCD, of course . . .)

- A typical nucleus has $A = 235$ (uranium), and is **unstable**, i.e., it will break apart. Moreover, the $A$-body problem requires numerical methods for differential equations in $L^2(\mathbb{R}^{705})^4$ . . .
Quantum dots

Quantum dots are very similar to atoms:

- $N$ Electrons (pseudo-)confined to stay in a bounded region $\Omega$ in $\mathbb{R}^d$, where $d < 3$ is possible due to same confinement.
- Typically manufactured via etching processes on semiconductor bulk.

Figure: Standard “vertical quantum dot” where electrons are confined in a small region marked “Dot”. The source and drain are electrodes that allow loading and unloading electrons to the pseudo-two-dimensional region.
Quantum rings and wires

These are quantum dots where the manifold of constraint is to a good approximation 1-dimensional. Hence, configuration space is typically $S^1$, which gives Hilbert spaces of periodic functions, or some other curve in $\mathbb{R}^3$.

Figure: Electron microscope image of a fabricated quantum wire. The diameter is about 400 nm.
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