

Theorem: The func. Ψ_k and ϕ_k defined above

coincide. They form a complete orthonormal set in $L^2(\mathbb{R})$ and are the eigenfunc. of the quantum harmonic oscillator hamiltonian ($H = \frac{1}{2}(p^2 + q^2)$).

Proof: By construction, it is clear that

ϕ_k are oscillator eigenfunctions to $EV k + \frac{1}{2}$.

H self-adjoint $\Rightarrow H_k$ are orthogonal:

$$\begin{aligned} \langle \phi_k | H \phi_j \rangle &= \lambda_j \langle \phi_k | \phi_j \rangle = \\ &= \langle H \phi_k | \phi_j \rangle = \bar{\lambda}_k \langle \phi_k | \phi_j \rangle = \lambda_k \langle \phi_k | \phi_j \rangle \end{aligned}$$

i.e. $\lambda_k \neq \lambda_j \Rightarrow \phi_k \perp \phi_j$.

$$\begin{aligned} \lambda_k \text{ real}; \quad \langle \phi_k | H \phi_k \rangle &= \lambda_k \| \phi_k \|^2 \\ &= \langle H \phi_k | \phi_k \rangle = \bar{\lambda}_k \| \phi_k \|^2 \Rightarrow \lambda_k = \bar{\lambda}_k \end{aligned}$$

From recurrence $\Rightarrow \phi_k = P_k(x) e^{-\frac{x^2}{2}}$, $P_k(x)$ - poly of degree k

By orthogonality $\Rightarrow P_k(x)$ must be multiple of H_k (Hermite polynomial of degree k).

Proof of completeness: [25, §7.8].

Visualization: [25, p. 168; CD 5.3-5.9]

shows the time evolution of the superpositions of eigen states

III Model Reductions

III.1 The Molecular Hamiltonian

$$i\dot{\psi} = H_{\text{mol}} \psi,$$

$$H_{\text{mol}} = T + V, T = T_N + T_e, V = V_{NN} + V_{Ne} + V_{ee}.$$

N nuclei of masses $M_n, n=1, \dots, N$,

electric charges $Z_n e, n=1, \dots, N, Z_n \in \mathbb{N}$

positions $X_n \in \mathbb{R}^3, n=1, \dots, N, X = (x_1, \dots, x_N)$

L electrons of mass m , charge $-e$

positions $y_e \in \mathbb{R}^3, e=1, \dots, L, y = (y_1, \dots, y_L)$

$$\rightsquigarrow V_{NN}(x) = \sum_{1 \leq k < n \leq N} \frac{Z_k Z_n e^2}{|x_k - x_n|},$$

$$V_{Ne}(x, y) = - \sum_{e=1}^L \sum_{n=1}^N \frac{Z_n e^2}{|y_e - x_n|},$$

$$V_{ee}(y) = \sum_{1 \leq j < e \leq L} \frac{e^2}{|y_j - y_e|}.$$

$$T_N = - \sum_{n=1}^N \frac{\hbar^2}{2M_n} \Delta_{x_n}, T_e = - \sum_{e=1}^L \frac{\hbar^2}{2m} \Delta_{y_e}.$$

Remark: Atomic units, $\hbar = 1, e = 1, m = 1$.

Theorem: H_{mol} is self-adjoint with domain H^2 .

Proof: [19, Thm. X.16].

Indistinguishable particles:

Wave function for two identical particles satisfies for

$$R\psi(x_1, x_2; t) := \psi(x_2, x_1; t)$$

that the average of any observable A remains unchanged under exchange of two particles;

$$\langle R\psi | A | R\psi \rangle = \langle \psi | A | \psi \rangle \quad (*)$$

where A is a self-adjoint operator ("observable")

Decomposition of ψ into its symmetric and antisymmetric part, $\psi = \psi_+ + \psi_-$.

$$\begin{aligned} \text{Remark: } \psi(x_1, x_2; t) &= \frac{1}{2} [\psi(x_1, x_2; t) + \psi(x_2, x_1; t)] + \\ &\quad + \frac{1}{2} [\psi(x_1, x_2; t) - \psi(x_2, x_1; t)] \end{aligned}$$

$$\text{Thus, } R\psi_+ = \psi_+, \quad R\psi_- = -\psi_-,$$

$$\psi_+ = \frac{1}{2} (\psi + R\psi), \quad \psi_- = \frac{1}{2} (\psi - R\psi)$$

From $(*)$ it follows that $\text{Re} \langle \psi_+ | A | \psi_- \rangle = 0$, since:

$$\begin{aligned} \text{Re} \langle \psi_+ | A | \psi_- \rangle &= \frac{1}{2} (\overline{\langle \psi_+ | A | \psi_- \rangle} + \overline{\langle \psi_+ | A | \psi_- \rangle}) = \\ &= \frac{1}{2} (\langle \psi_+ | A | \psi_- \rangle + \langle \psi_- | A | \psi_+ \rangle) = \frac{1}{4} (\langle \psi_+ | A | \psi_- \rangle + \langle \psi_- | A | \psi_+ \rangle) \\ &\quad + \langle \psi_- | A | \psi_+ \rangle) = \\ &= \frac{1}{4} (\cancel{\langle \psi | A | \psi \rangle} + \cancel{\langle R\psi | A | \psi \rangle} - \cancel{\langle \psi | A | R\psi \rangle} - \cancel{\langle R\psi | A | R\psi \rangle} \\ &\quad + \cancel{\langle \psi | A | \psi \rangle} - \cancel{\langle R\psi | A | \psi \rangle} + \cancel{\langle \psi | A | R\psi \rangle} - \cancel{\langle R\psi | A | R\psi \rangle}) \\ &= 0. \end{aligned}$$

M shows out that

$$\operatorname{Re} \langle \psi_+ | A | \psi_- \rangle = 0 \Rightarrow \psi_+ = 0 \vee \psi_- = 0$$

Proof: Set $A\psi := \langle \psi | \psi_+ \rangle \psi_- + \langle \psi | \psi_- \rangle \psi_+$,
 $\psi \in D(A)$.

$$\begin{aligned} \text{Then } \langle \psi_1 | A \psi_2 \rangle &= \langle \psi_1 | \langle \psi_2 | \psi_+ \rangle \psi_- + \langle \psi_2 | \psi_- \rangle \psi_+ \rangle \\ &= \langle \psi_1 | \psi_- \rangle \langle \psi_2 | \psi_+ \rangle + \langle \psi_1 | \psi_+ \rangle \langle \psi_2 | \psi_- \rangle = \\ &= \langle \langle \psi_- | \psi_1 \rangle \psi_2 | \psi_+ \rangle + \langle \langle \psi_+ | \psi_1 \rangle \psi_2 | \psi_- \rangle \\ &= \langle A\psi_1 | \psi_2 \rangle \Rightarrow A \text{ is self-adjoint} \end{aligned}$$

$$\begin{aligned} \operatorname{Re} \langle \psi_+ | A | \psi_- \rangle &= \operatorname{Re} (|\langle \psi_+ | \psi_- \rangle|^2 + \|\psi_+\|^2 \|\psi_-\|^2) \\ &= |\langle \psi_+ | \psi_- \rangle|^2 + \|\psi_+\|^2 \|\psi_-\|^2 (\geq 0) \\ &= 0 \text{ iff } \psi_+ = 0 \vee \psi_- = 0 \end{aligned}$$

Thus, there are only two possibilities:

Symmetry or antisymmetry

$$\Psi(x_2, x_1; t) = \Psi(x_1, x_2; t) \quad (\text{for bosons})$$

$$\text{or } \Psi(x_2, x_1; t) = -\Psi(x_1, x_2; t) \quad (\text{for fermions})$$

Antisymmetry holds for: electrons, protons, neutrons

These furthermore obey the

Pauli exclusion principle: (W. Pauli, 1925):

Like particles cannot simultaneously be in the same quantum state.

Antisymmetry $\Rightarrow \Psi(x, x; t) = 0$, s.t. two identical fermions cannot be at the same position at the same time.

Product states can be antisymmetrized:

$$\Psi(x_1, x_2; t) = \frac{1}{\sqrt{2}} (\varphi_1(x_1; t) \varphi_2(x_2; t) - \varphi_1(x_2; t) \varphi_2(x_1; t))$$

Or more generally, as a Slater determinant

$$\Psi(x_1, \dots, x_N; t) = \frac{1}{\sqrt{N!}} \det (\varphi_j(x_n; t))_{j,n=1}^N$$

Cost of dimensionality: f particles in \mathbb{R}^3 , 2-grid

points per coordinate, yields 2^{3f} grid points.

CO_2 molecule: 3 nuclei, 22 electrons $\rightarrow 2^{75}$ points,

8 byte memory for double precision float $\rightarrow 2^{75} \cdot 8 \text{ bytes} \approx 10^{23}$ b

3.2 Variational approximations

Consider abstract Schrödinger equation

$$i\dot{\Psi} = H\Psi, \quad \Psi(0) = \Psi_0. \quad (1)$$

\mathcal{H} ... complex Hilbert space

M ... submanifold of \mathcal{H} ,

$T_m M$... tangent space to M in the point m

(This is represented by the linear hull of the derivatives of all differentiable paths on M passing through m)

We seek an approximation $\Psi \approx \Psi_0 \in M$ for (1).

m is defined by a variational principle:

Determine $\Psi_0 \in M$ such that $v \in T_m M$ satisfies

$$v \in T_m M \quad \text{s.t.} \quad \langle v | i\dot{\Psi}_0 - \frac{1}{i} H \Psi_0 \rangle = 0 \quad \forall v \in T_m M. \quad (2)$$

For the subsequent arguments, assume that

$T_m M$ is a complex linear space

Thus, it is sufficient to require either

$$\operatorname{Re} \langle v | i\dot{\Psi}_0 - \frac{1}{i} H \Psi_0 \rangle = 0 \quad \text{or}$$

$$\operatorname{Im} \langle v | i\dot{\Psi}_0 - \frac{1}{i} H \Psi_0 \rangle = 0$$

in (2).

Remark: (2) can be seen as a Galerkin

condition on the state-dependent approximation space $\mathcal{T}_M M$

Remark: (2) carries points with the minimum

condition for the following linear approximation problem:

Choose $w = ii$ as that $w \in \mathcal{T}_M M$ for which

$$\|w - \frac{1}{i} H_M\| \text{ is minimal.}$$

In other words: ii is the orthogonal projection

of $\frac{1}{i} H_M$ onto the tangent space $\mathcal{T}_M M$. See [29]

Denote the orthogonal projector onto $\mathcal{T}_M M$ by $P(M)$, then

$$ii = P(M) \frac{1}{i} H_M \quad (3)$$

Remark: $P(M)$ is not complex linear in general.

Remark: (3) is a nonlinear PDE in general.

Remark: Existence of a solution i of (3) can only be verified with further assumptions on the operator H and manifold M .