Exercise 1

Quantum chemistry (TKJ4170)

1 Dirac bra-ket notation and the inner product of square integrable functions.

The scalar product (inner-product) of two square integrable functions of x, $\psi_m(x)$ and $\psi_n(x)$ is

$$\langle \psi_m | \psi_n \rangle = \langle m | n \rangle = \int_{-\infty}^{\infty} \psi_m^*(x) \psi_n(x) \mathrm{d}x, \tag{1}$$

where * denotes the complex conjugate. Show that

a) $\langle \psi_m | \psi_n \rangle = \langle \psi_n | \psi_m \rangle^*$

b) for a constant c, $\langle c\psi_m | \psi_n \rangle = c^* \langle \psi_m | \psi_n \rangle$ and $\langle \psi_m | c\psi_n \rangle = c \langle \psi_m | \psi_n \rangle$

c) $\langle \psi_m | \psi_n + \psi_o \rangle = \langle \psi_m | \psi_n \rangle + \langle \psi_m | \psi_o \rangle$

by using the definition in (1).

d) Express the integral $\int \psi_m^*(x)\, \Omega\, \psi_n(x)\, dx$, where Ω is an operator, in bra-ket notation.

2 Properties of Hermitian operators

Let Ω be a Hermitian operator that satisfies

$$\Omega\, \psi_n = \omega_n\, \psi_n, \quad n = 1, 2, \ldots, M, \tag{2}$$

and assume that the $\{\psi_n\}$ are normalized.

a) What is the definition of a Hermitian operator?

b) Prove that the eigenvalues of Hermitian operators are real

c) Prove that for $\omega_i \neq \omega_j$, $\langle \psi_i \,|\, \psi_j \rangle = 0$

3 Measurement of observables.

Again, let Ω be a Hermitian operator that satisfies

$$\Omega\, \psi_n = \omega_n\, \psi_n, \quad n = 1, 2, \ldots, M, \tag{3}$$

and assume that ψ_n are normalized. Since $\{\psi_n : n = 1, 2, \ldots, M\}$ is a complete set, a function Φ can be expressed as

$$\Phi = \sum_{n=1}^{M} c_n\, \psi_n, \tag{4}$$

for some set of $\{c_n\}$. Assume that Φ is normalized.

a) Express $\langle \Phi \,|\, \Omega \,|\, \Phi \rangle$ in terms of c_n and ω_n.

b) Suppose a system is prepared in the state Φ. Which values of the observable Ω can be obtained in an experiment?

c) What is mean value of the measurements of the observable Ω for systems prepared in the state Φ. Give the answer in terms of c_n and ω_n.

Let Ψ be an eigenfunction of both Ω_1 and Ω_2, that is,

$$\Omega_1\, \Psi = f_1\, \Psi, \quad \Omega_2\, \Psi = f_2\, \Psi. \tag{5}$$

d) Show that this implies that $[\Omega_1, \Omega_2]\, \Psi = 0$.

e) What does this result imply when it comes to measurement of the observables represented by Ω_1 and Ω_2?

4 Overlap matrix

Consider a set of square integrable functions $\{\phi_n : n = 1, 2, \ldots, K\}$ that are normalized but not necessarily orthogonal.

a) What is $\langle \phi_m \,|\, \phi_n \rangle$?

b) It is often useful to use matrix notation for integrals. How would you define a matrix containing the integrals $\langle \phi_m \,|\, \phi_n \rangle$?

c) Can we say anything about the magnitude of $\langle \phi_m \,|\, \phi_n \rangle$?

d) If the functions ϕ_n are real-valued, what properties does this matrix have?

e) If the functions are orthonormal, what does this matrix become?

5 Matrix representation of operators

Consider an orthonormal set of square integrable functions $\{f_n : n = 1, 2, \ldots, K\}$, and an operator Ω that acts on such functions.

Define the matrix representation of Ω in the basis $\{f_n\}$. What dimensions does this matrix have?

Let $\{e_n : n = 1, 2, \ldots, K\}$ be another orthonormal basis, spanning the same space as $\{f_n\}$.

a) Define the matrix representation of Ω in the basis $\{e_n\}$

b) Express e_i in terms of the $\{f_n\}$

c) Determine the transformation matrix which takes us between the two representations of Ω