Solution exercise 1

Quantum chemistry (TKJ4170)

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

a)

$$\begin{aligned}
\langle \psi_m | \psi_n \rangle &= \int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\mathrm{d}x \\
&= \int_{-\infty}^{\infty} (\psi_m(x)\psi_n^*(x))^*\mathrm{d}x \\
&= \left(\int_{-\infty}^{\infty} \psi_m(x)\psi_n^*(x)\mathrm{d}x \right)^* \\
&= \left(\int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x)\mathrm{d}x \right)^* = \langle \psi_n | \psi_m \rangle^*
\end{aligned}$$

b)

$$\begin{aligned}
\langle c\psi_m | \psi_n \rangle &= \int_{-\infty}^{\infty} (c\psi_m(x))^*\psi_n(x)\mathrm{d}x \\
&= c^* \int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\mathrm{d}x = c^*\langle \psi_m | \psi_n \rangle
\end{aligned}$$

$$\begin{aligned}
\langle \psi_m | c\psi_n \rangle &= \int_{-\infty}^{\infty} \psi_m^*(x)(c\psi_n(x))\mathrm{d}x \\
&= c \int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)\mathrm{d}x = c\langle \psi_m | \psi_n \rangle
\end{aligned}$$

c)

$$\begin{aligned}\langle\psi_m|\psi_n+\psi_o\rangle &= \int_{-\infty}^{\infty}\psi_m^*(x)(\psi_n(x)+\psi_o(x))\mathrm{d}x\\ &= \int_{-\infty}^{\infty}\psi_m^*(x)\psi_n(x)+\psi_m^*(x)\psi_o(x)\mathrm{d}x\\ &= \int_{-\infty}^{\infty}\psi_m^*(x)\psi_n(x)\mathrm{d}x+\int_{-\infty}^{\infty}\psi_m^*(x)\psi_o(x)\mathrm{d}x = \langle\psi_m|\psi_n\rangle+\langle\psi_m|\psi_o\rangle\end{aligned}$$

d)

$$\int_{-\infty}^{\infty}\psi_m^*(x)\Omega\psi_n(x)\mathrm{d}x = \int_{-\infty}^{\infty}\psi_m^*(x)(\Omega\psi_n(x))\mathrm{d}x = \langle\psi_m|\Omega\psi_n\rangle = \langle\psi_m|\Omega|\psi_n\rangle$$

2 Properties of Hermitian operators

a) The definition of a Hermitian operator, is an operator which satisfies

$$\langle\psi_m|\Omega|\psi_n\rangle = \langle\psi_n|\Omega|\psi_m\rangle^*.$$

b) We have

$$\langle\psi_n|\Omega|\psi_n\rangle = \omega_n\langle\psi_n|\psi_n\rangle = \omega_n \tag{1}$$

but also

$$\langle\psi_n|\Omega|\psi_n\rangle = \langle\psi_n|\Omega|\psi_n\rangle^* = \omega_n^*\langle\psi_n|\psi_n\rangle^* = \omega_n^* \tag{2}$$

where we have used the hermicity of Ω for the first equality. Putting (1) equal to (2) we obtain

$$\omega_n = \omega_n^*$$

which means that ω_n must be real.

c) We have

$$\langle\psi_m|\Omega|\psi_n\rangle = \omega_n\langle\psi_m|\psi_n\rangle, \tag{3}$$

but using the hermicity of Ω we may also write

$$\langle\psi_m|\Omega|\psi_n\rangle = \langle\psi_n|\Omega|\psi,\rangle^* = \omega_m^*\langle\psi_n|\psi_m\rangle^* = \omega_m\langle\psi_m|\psi_n\rangle, \tag{4}$$

where we in the last equality use that ω_m is real (derived in the previous problem) and that $\langle\psi_m|\psi_n\rangle = \langle\psi_n|\psi_m\rangle^*$ which we proved in 1a).

Setting (3) equal to (4) we obtain

$$\begin{aligned}\omega_n\langle\psi_m|\psi_n\rangle &= \omega_m\langle\psi_m|\psi_n\rangle\\ (\omega_n-\omega_m)\langle\psi_m|\psi_n\rangle &= 0\end{aligned}$$

and as $\omega_m \neq \omega_n \implies \omega_n - \omega_m \neq 0$, we must have $\langle\psi_m|\psi_n\rangle = 0$.

3 Measurement of observables.

a)

$$\begin{aligned}\langle \Phi \,|\, \Omega \,|\, \Phi \rangle &= \sum_{m,n} c_m^* c_n \langle \psi_m \,|\, \Omega \,|\, \psi_n \rangle \\ &= \sum_{m,n} c_m^* c_n \omega_n \langle \psi_m \,|\, \psi_n \rangle = \sum_{m,n} c_m^* c_n \omega_n \delta_{m,n} = \sum_n |c_n|^2 \omega_n\end{aligned}$$

b) When doing a single measurement of the observable, one of the eigenvalues of the operator is meassured. ω_n is measured with a probability $|c_n|^2$.

c) The average value measured for a collection of identical and identically prepared systems in Φ is given by $\langle \Omega \rangle = \langle \Phi \,|\, \Omega \,|\, \Phi \rangle$. It is the weighted sum of the eigenvalues where the probabilities $|c_n|^2$, the probability of measuring an eigenvalue in a single measurement is the square modulus of the expansion coefficient of the wavefunction.

d)

$$\begin{aligned}[\Omega_1, \Omega_2]\Psi &= \Omega_1\Omega_2\Psi - \Omega_2\Omega_1\Psi \\ &= \Omega_1 f_2 \Psi - \Omega_2 f_1 \Psi \\ &= f_2 \Omega_1 \Psi - f_1 \Omega_2 \Psi \\ &= f_2 f_1 \Psi - f_1 f_2 \Psi \\ &= (f_1 f_2 - f_1 f_2)\Psi = 0\end{aligned}$$

e) This implies that the observables Ω_1 and Ω_2 may be measured simultaneously with arbitrary precision.

4 Overlap matrix

a) This is the overlap between the functions ϕ_m and ϕ_n. It is a measure of similarity between the two functions.

b) $S_{mn} = \langle \phi_m \,|\, \phi_n \rangle$

c) The maximum magnitude of the element $\langle \phi_m \,|\, \phi_n \rangle = S_{mn}$ is 1 ($\phi_m = \phi_n \implies S_{mn} = 1$, $\phi_m = -\phi_n \implies S_{mn} = -1$, $\phi_m = \mathrm{i}\phi_n \implies S_{mn} = -\mathrm{i}$, and , $\phi_m = -\mathrm{i}\phi_n \implies S_{mn} = \mathrm{i}$). If they are orthogonal then $\langle \phi_n \,|\, \phi_m \rangle = 0$ (minimum).

d) We know from previously that for general complex square integrable functions $\langle \phi_m \,|\, \phi_n \rangle = \langle \phi_n \,|\, \phi_m \rangle^*$, if these functions are real we have $\langle \phi_n \,|\, \phi_m \rangle^* = \langle \phi_n \,|\, \phi_m \rangle$ so that $S_{mn} = S_{nm}$

e) The identity matrix.

5 Matrix representation of operators

We define the matrix

$$\Omega^f_{nm} = \langle f_n | \Omega | f_m \rangle = \int_{-\infty}^{\infty} f_m^* f_n \mathrm{d}\tau$$

$\boldsymbol{\Omega}^f$ is an $K \times K$ matrix.

a) $\Omega^e_{nm} = \langle e_n | \Omega | e_m \rangle$

b) Since the bases span the same space, we can write $e_i = \sum_n c_{ni} f_n$

c) Inserting the result in b) into a):

$$\Omega^e_{ij} = \sum_{nm} c^*_{ni} \langle f_n | \Omega | f_m \rangle c_{mj}.$$

Which can be written in matrix form,

$$\Omega^e_{ij} = [\boldsymbol{C}^\dagger \boldsymbol{\Omega}^f \boldsymbol{C}]_{ij},$$

where $\boldsymbol{C}$ is the unitary matrix transforming between the two bases. Note that $\boldsymbol{C}^\dagger$ is the conjugate transpose of $\boldsymbol{C}$.