Chem675 Homework 01

Group Name: Scholars
Chengwei, Peter, Dylan, Haejung, Dolimar

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Le problems:

1. **Identify the normalization condition that describes a wavefunction $\Phi(x)$ expanded in terms of a complete orthonormal set of basis functions $\{\phi_i(x)\}$ with coefficients $\{c_i\}$.**

$$1 = \int \Phi^* \Phi d\tau$$

$$= \int d\tau (c_1\phi_1 + c_2\phi_2 + ...c_n\phi_n)^*(c_1\phi_1 + c_2\phi_2 + ...c_n\phi_n)$$

$$= \int d\tau \sum_i c_i^* \phi_i^* \sum_j c_j \phi_j = \int d\tau \sum_i \sum_j c_i^* \phi_i^* c_j \phi_j$$

$$= \sum_i \sum_j c_i^* c_j \int d\tau \phi_i^* \phi_j$$

Since $\phi_i(x)$ is orthonormal

$$= \sum_i \sum_j c_i^* c_j \delta_{ij} = \sum_i c_i^* c_i \times 1 = \sum_i |c_i|^2$$

$$\sum_i |c_i|^2 = 1$$

2. **Consider the wavefunction $\Psi(x) = 0.6i\phi_1(x) + 0.1\phi_2(x) + c_3\phi_3(x) - 0.5\phi_4(x)$ where $\Psi(x)$ is normalized, $\hat{O}\phi_j = j\phi_j(x)$ and $\{\phi_j(x)\}$ form an orthonormal set.**

   - **Calculate the magnitude of c_3.**

$$\langle \hat{O} \rangle = \int \Psi^* \hat{O} \Psi d\tau$$

$$= \int d\tau (0.6\phi_1(x) + 0.1\phi_2(x) + c_3\phi_3(x) + ...$$

$$(-0.5)\phi_5(x))^* \hat{O} \left(0.6\phi_1(x) + 0.1\phi_2(x) + c_3\phi_3(x) + (-0.5)\phi_5(x)\right)$$

Since $\Psi(x)$ is orthonormal (and normalized)

$$\sum_i |c_i|^2 = 1$$

$$\therefore$$

$$\sum_i |c_i|^2 = 0.6i^2 + 0.1^2 + c_3^2 + (-0.5)^2 = 1$$

$$|c_3|^2 = 0.38$$

for posterity:

$$\sqrt{1 - (0.6i^2 + 0.1^2 + (-0.5)^2)} = c_3$$

$$c_3 = 0.61_{644140} \approx 0.62$$

- **Plot the expected distribution of the outcomes of repeated measurements of the operator $\hat{O}$**

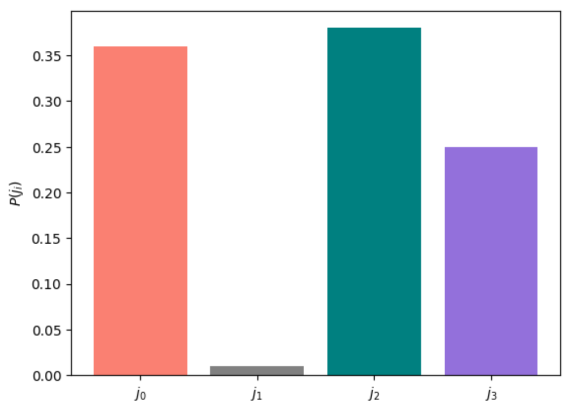

Figure 1: Plot of the probability of getting the eigenvalue j_i in a measurement of the property O

- **Compute $\langle \hat{O} \rangle$**

$$\langle \hat{O} \rangle = \int \Psi^* \hat{O} \Psi d\tau$$

vide supra

$$= \int d\tau \sum_i c_i^* \phi_i^* \hat{O} \sum_j c_j \phi_j$$

$$= \sum_i \sum_j c_i^* c_j \int d\tau \phi_i^* \hat{O} \phi_j$$

where ϕ_i is an eigenfunction and $\hat{O}\phi_j(x) = j\phi_j(x)$

$$= \sum_i \sum_j c_i^* c_j \int d\tau \phi_i^* j \phi_j = \sum_i \sum_j c_i^* c_j j_j \int d\tau \phi_i^* j \phi_j$$

and $\int d\tau \phi_i^* j \phi_j = \delta_{ij}$, hence:

$$= \sum_i \sum_j c_i^* c_j j_j \delta_{ij} = \sum_i \sum_j c_i^* c_j j_j$$

$$\langle O \rangle = \sum_i |c|^2 j_i$$

where

$$\sum_i |c|^2 = 1$$

$$\therefore$$

$$\langle O \rangle = \sum_{j_i} P_{j_i} j_i$$

$$\langle O \rangle = 1|0.6i|^2 + 2|0.1|^2 + 3(0.38) + 4|-0.5|^2 = 2.52$$

3. **Prove Hermitian operators only have real eigenvalues.**

Let $\hat{\Diamond}$ be a linear hermitian operator representing the physical quantity $\Diamond$

$$\therefore$$

$$\int \xi_i^* \hat{\Diamond} \xi_i d\tau = \int \xi_i \left(\hat{\Diamond} \xi_i \right)^* d\tau$$

where $\{\xi_i\}$ are orthonormal eigenfunctions of $\hat{\Diamond}$ satisfying: $\hat{\Diamond}\xi_i = \varepsilon_i \xi_i$

$$\int \xi_i^* \varepsilon_i \xi_i d\tau = \int \xi_i \left(\varepsilon_i \xi_i \right)^* d\tau$$

$$\int \xi_i^* \varepsilon_i \xi_i d\tau = \int \xi_i \varepsilon_i^* \xi_i^* d\tau$$

$$\varepsilon_i \int \xi_i^* \xi_i d\tau = \varepsilon_i^* \int \xi_i \xi_i^* d\tau$$

where $\xi_i \xi_i^* = |\xi_i|^2$

$$\therefore$$

$$\varepsilon_i \int |\xi_i|^2 d\tau = \varepsilon_i^* \int |\xi_i|^2 d\tau$$

$$\varepsilon_i \int |\xi_i|^2 d\tau - \varepsilon_i^* \int |\xi_i|^2 d\tau = 0$$

$$(\varepsilon_i - \varepsilon_i^*) \int |\xi_i|^2 d\tau = 0$$

$$(\varepsilon_i - \varepsilon_i^*) = 0$$

Furthermore:

$$\varepsilon_i = \varepsilon_i^*$$

Therefore all eigenvalues must be $\in \mathbb{R}$

Alternative:

Let $\hat{A}$ be a Hermitian operator, and corresponding orthonormal eigenstates are $|\phi_i\rangle$, by definition,

$$\hat{A}\,|\phi_i\rangle = \varepsilon_i\,|\phi_i\rangle \tag{1}$$

where ε_i are eigenvalues. ($i = 1, 2, \ldots$). Consider a certain i.

Conjugate transpose on both sides:

$$\langle\phi_i|\,\hat{A}^\dagger = \varepsilon_i^*\,\langle\phi_i| \tag{2}$$

right-multiply $|\phi_i\rangle$ to (2):

$$\langle\phi_i|\,\hat{A}^\dagger\,|\phi_i\rangle = \varepsilon_i^*\,\langle\phi_i|\phi_i\rangle = \varepsilon_i^* \tag{3}$$

left-multiply $\langle\phi_i|$ to (1):

$$\langle\phi_i|\,\hat{A}\,|\phi_i\rangle = \varepsilon_i\,\langle\phi_i|\phi_i\rangle = \varepsilon_i \tag{4}$$

Since $\hat{A}$ is Hermitian, $\hat{A}^\dagger = \hat{A}$, so the l.h.s. of (3)(4) are equal. Therefore,

$$\varepsilon_i^* = \varepsilon_i$$

so all eigenvalues ε_i are real.

4. **Complete Python exercise problemset1.ipynb.**

```python
x = np.linspace(-10,10,200);
y_1 = lambda x: ((1/np.pi)**(1/4))*np.exp((-1*x**2)/2)
y_2 = lambda x: ((4/np.pi)**(1/4))*x*np.exp((-1*x**2)/2)
fig, ax = plt.subplots()
ax.plot(x,y_1(x),color='aqua')
ax.plot(x,y_2(x),color='salmon')
ax.set_xlabel(r"Position $/ x$")
ax.set_ylabel(r"$\psi_i(x)$")
ax.set_xlim([-5,5])
plt.legend([r'$\psi_0$',r'$\psi_1$'])

```

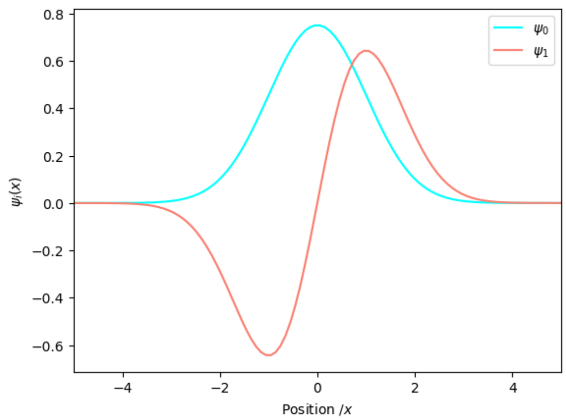

Figure 2: Plot of $\Psi_0(x)$ and $\Psi_1(x)$

```
x=symbols('x')
psi_1 = ((1/pi)**(1/4))*exp((-1*x**2)/2)
psi_2 = ((4/pi)**(1/4))*x*exp((-1*x**2)/2)
```

$$? = \int \psi_i^* \psi_j \text{ when } i \neq j$$

```
print(f"Result: {integrate(psi_2.conjugate()*psi_1,(x,-np.inf,np.inf))}")
print(f"Result: {integrate(psi_1.conjugate()*psi_2,(x,-np.inf,np.inf))}")
>> Result: 0
>> Result: 0
```

$$? = \int \psi_i^* \psi_j \text{ when } i = j$$

```
print(f"Result: {integrate(psi_1.conjugate()*psi_1,(x,-np.inf,np.inf))}")
print(f"Result: {integrate(psi_2.conjugate()*psi_2,(x,-np.inf,np.inf))}")
>> Result: 1
>> Result: 1
```

$$\therefore \int \psi_i^* \psi_j = \delta_{ij}$$