

Quantum Chemistry

Corrections 2A

1. Write out the operator \hat{A}^2 for

$$(a) \hat{A} = \frac{d^2}{dx^2}$$

$$(b) \hat{A} = \frac{d}{dx} + x$$

$$(c) \hat{A} = \frac{d^2}{dx^2} - 2x \frac{d}{dx} + 1$$

(Hint: Make sure to operate on a function rather than simply squaring the operator).

We have to apply two times the operator \hat{A} on a function $f(x)$ to determine the square of the operator.

$$(a) \left(\frac{d^2}{dx^2} \right)^2 f(x) = \left(\frac{d^2}{dx^2} \right) \left(\frac{d^2 f(x)}{dx^2} \right) = \frac{d^4 f(x)}{dx^4} \Rightarrow \left(\frac{d^2}{dx^2} \right)^2 = \frac{d^4}{dx^4}$$

$$(b) \left(\frac{d}{dx} + x \right)^2 f(x) = \left(\frac{d}{dx} + x \right) \left(\frac{df(x)}{dx} + xf(x) \right) = \frac{d}{dx} \left(\frac{df(x)}{dx} + xf(x) \right) + x \left(\frac{df(x)}{dx} + xf(x) \right) \\ = \frac{d^2 f(x)}{dx^2} + f(x) + x \frac{df(x)}{dx} + x^2 f(x) \\ \Rightarrow \left(\frac{d}{dx} + x \right)^2 = \frac{d^2}{dx^2} + 2x \frac{d}{dx} + x^2 + 1$$

$$(c) \left(\frac{d^2}{dx^2} - 2x \frac{d}{dx} + 1 \right)^2 f(x) = \left[\frac{d^2}{dx^2} \right] \left[2x \frac{d}{dx} \right] \left[1 \right] \left(\frac{d^2 f(x)}{dx^2} - 2x \frac{df(x)}{dx} + f(x) \right) \\ = \boxed{\frac{d^4 f(x)}{dx^4} - 2 \frac{d}{dx} \left(\frac{df(x)}{dx} + x \frac{d^2 f(x)}{dx^2} \right) + \frac{d^2 f(x)}{dx^2}} + \boxed{2x \frac{d^3 f(x)}{dx^3} + 4x \left(\frac{df(x)}{dx} + x \frac{d^2 f(x)}{dx^2} \right) - 2x \frac{df(x)}{dx}} + \boxed{\frac{d^2 f(x)}{dx^2} - 2x \frac{df(x)}{dx} + f(x)} \\ = \boxed{\frac{d^4 f(x)}{dx^4} - 2 \frac{d^2 f(x)}{dx^2} - 2 \frac{d^3 f(x)}{dx^3} - 2x \frac{d^3 f(x)}{dx^3}} + 2 \boxed{\frac{d^3 f(x)}{dx^3}} - 2x \frac{d^3 f(x)}{dx^3} + 4x \frac{df(x)}{dx} + 4x^2 \frac{d^2 f(x)}{dx^2} - 4x \boxed{\frac{df(x)}{dx}} + \boxed{f(x)} \\ \Rightarrow \left(\frac{d^2}{dx^2} - 2x \frac{d}{dx} + 1 \right)^2 = \frac{d^4}{dx^4} - 4x \frac{d^3}{dx^3} + (4x^2 - 2) \frac{d^2}{dx^2} + 1$$

2. The model of a particle in a one-dimensional box has been applied to the π electrons in linear conjugated hydrocarbons. Consider butadiene, $H_2C=CH-CH=CH_2$, which has four π electrons. Although butadiene is not a linear molecule, we shall assume for simplicity that the π electrons in butadiene move along a straight line whose length can be estimated as equal to two $C=C$ bond lengths, or $2 \times 1.35 \text{ \AA}$, plus one $C-C$ bond, or 1.54 \AA , plus the distance of a carbon atom radius at each end, or another 1.54 \AA , for a total of

5.78Å. The Pauli Exclusion Principle (which we shall discuss later, but should be familiar from first year chemistry) says that each state can contain only two electrons (with opposite spins). This implies that the four π electrons fill the first two levels of the particle in the box. Use this information to determine what wavelength this molecule would absorb if one uses light to induce a transition to the lowest excited state (i.e., what is the lowest energy transition to a higher state). Express this value both as wavelength and as wavenumber ($1/\lambda$ in units of cm^{-1}).

Because of the Pauli principle (to be discussed in detail later in the course) the 4 π electrons of butadiene occupy the two lowest energy levels of the particle-in-a-box problem. The lowest energy transition corresponds therefore to the excitation of an electron from the 2nd to the 3rd energy level. According to the Bohr correspondence principle the transition energy equals the difference in energy between these two levels. As seen in class, the energy of level n of a particle with mass m (here the electron) in a box of length a (here the length of the molecule) is given by:

$$E_n = \frac{n^2 h^2}{8ma^2}$$

The energy of the transition is thus:

$$\Delta E_{3 \leftarrow 2} = E_3 - E_2 = \frac{h^2}{8ma^2} (3^2 - 2^2) = \frac{5h^2}{8ma^2}$$

One then calculates $\tilde{\nu}$ et λ according to:

$$\begin{aligned} \Delta E_{3 \leftarrow 2} = h\nu = hc\tilde{\nu} &= \frac{5h^2}{8ma^2} \quad \Rightarrow \quad \tilde{\nu} = \frac{5h}{8mca^2} = 45390 \text{ cm}^{-1} \\ &\Rightarrow \lambda = \frac{1}{\tilde{\nu}} = 220.31 \text{ nm} \end{aligned}$$

This corresponds to UV light.

3. Using the trigonometric identity

$$\sin \alpha \sin \beta = \frac{1}{2} \cos(\alpha - \beta) - \frac{1}{2} \cos(\alpha + \beta)$$

show that the eigenfunctions of the particle-in-a-box Hamiltonian are orthonormal, i.e., they satisfy the relation

$$\int_0^a \psi_n^*(x) \psi_m(x) dx = \delta_{nm} \quad \text{where} \quad \delta_{nm} \begin{cases} 0 & \text{if } n \neq m \\ 1 & \text{if } n = m \end{cases}$$

If the above integral equals zero, we say that the set of functions is orthogonal, and if it equals to 1 we say that the set is normalized.

Given that the eigenfunctions of the particle-in-a-box problem are

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right)$$

we calculate:

$$\int_0^a \psi_n^*(x) \psi_m(x) dx = \frac{2}{a} \int_0^a \sin\left(\frac{n\pi}{a}x\right) \sin\left(\frac{m\pi}{a}x\right) dx = \frac{1}{a} \int_0^a \left[\cos\left(\frac{(n-m)\pi}{a}x\right) - \cos\left(\frac{(n+m)\pi}{a}x\right) \right] dx$$

For $n=m$ this yields:

$$\int_0^a \psi_n^*(x) \psi_m(x) dx = \frac{1}{a} \left[\int_0^a 1 \cdot dx - \underbrace{\left[\frac{a}{(n+m)\pi} \sin\left(\frac{(n+m)\pi}{a}x\right) \right]_0^a}_{=0} \right] = \frac{a}{a} = 1$$

While for $n \neq m$ this gives:

$$\int_0^a \psi_n^*(x) \psi_m(x) dx = \frac{1}{a} \left[\underbrace{\left[\frac{a}{(n-m)\pi} \sin\left(\frac{(n-m)\pi}{a}x\right) - \frac{a}{(n+m)\pi} \sin\left(\frac{(n+m)\pi}{a}x\right) \right]_0^a}_{=0} \right] = 0$$

Q.E.D