

1. Evaluate the commutators (assume a position representation)

a) $[\hat{x}, \hat{p}^2]$

b) $[\hat{p}, \hat{x}^2]$

c) $[\hat{p}, \hat{H}]$ where $\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$

2. *Quantization of Electromagnetic Waves.*

This is your first introduction to “Second Quantization” or a simple field theory, where the number particles in each state are also quantized. (First quantization is that the states themselves are quantized). Here the electromagnetic fields will be quantized into photons – the basis for explaining Einstein’s photoelectric effect.

Classically, a single-mode plane wave with wavenumber k (with $\omega = ck$) and the electric field linearly polarized along the x-axis can be written as (cgs units)

$$\vec{E}(\vec{r}, t) = A_k \cos(kz - \omega t) \vec{e}_x$$

$$\vec{B}(\vec{r}, t) = \frac{1}{c} A_k \cos(kz - \omega t) \vec{e}_y$$

or using complex notation and amplitudes

$$\vec{E}(\vec{r}, t) = \frac{1}{2} (A_k e^{i(kz - \omega t)} + A_k^* e^{-i(kz - \omega t)}) \vec{e}_x$$

$$\vec{B}(\vec{r}, t) = \frac{1}{2c} (A_k e^{i(kz - \omega t)} + A_k^* e^{-i(kz - \omega t)}) \vec{e}_y$$

We can quantize the amplitudes of the \vec{E} and \vec{B} fields with the mapping of the complex amplitudes to an operator $A_k \rightarrow \hat{A}_k$ and placing the system in a very large box of length L . We also restrict $k = m\pi/L$, $m \gg 1$ to make the normalization easier. Since \vec{E} and \vec{B} satisfy a differential equation of the same form as the harmonic oscillator, we might expect a similar structure and so we write the amplitude operators as proportional to dimensionless creation and annihilation operators with the same mathematical properties as in the harmonic oscillator, i.e.

$$\hat{A}_k = \sqrt{\frac{2\hbar\omega_k}{L}} \hat{a}_k, \hat{A}_k^\dagger = \sqrt{\frac{2\hbar\omega_k}{L}} \hat{a}_k^\dagger$$

where $\hat{a}_k, \hat{a}_k^\dagger$ are the creation and annihilation operators for a photon in the k^{th} mode. We assume the same commutation relationships as for the QHO:

$$[\hat{a}_k, \hat{a}_k^\dagger] = 1, [\hat{a}_k, \hat{a}_k] = 0, [\hat{a}_k^\dagger, \hat{a}_k^\dagger] = 0$$

(this assumption, as you will see in AEP 3620, will mean that photons are bosons)

a) Starting with $\vec{E}(\vec{r}, t) = \frac{1}{2} \sqrt{\frac{2\hbar\omega_k}{L}} (\hat{a}_k e^{i(kz - \omega t)} + \hat{a}_k^\dagger e^{-i(kz - \omega t)}) \vec{e}_x,$

$$\vec{B}(\vec{r}, t) = \frac{1}{2} \sqrt{\frac{2\hbar\omega_k}{L}} (\hat{a}_k e^{i(kz - \omega t)} + \hat{a}_k^\dagger e^{-i(kz - \omega t)}) \vec{e}_y,$$

find the energy of the electromagnetic wave with wavenumber k in the box of length L and unit cross-sectional area. Express this in terms of the number operator $\hat{n} = \hat{a}_k^\dagger \hat{a}_k$, i.e. express the intensity in terms of the number of photons in the k^{th} mode.
(Hint: The energy density is $\frac{1}{2}\epsilon_0|E(\vec{r})|^2 + \frac{1}{2}\epsilon_0c^2|B(\vec{r})|^2$ and integrate from 0 to L .)

- b) Is it possible to know both the value of the electric field and number of photons in the k^{th} mode at the same time? (hint: the operators for simultaneous observables commute. We will discuss this more later in class)
- c) Now that the electric field is quantized in amplitude, show that is no net electric field in the ground state, i.e. $\langle 0 | \hat{E} | 0 \rangle = 0$.
- d) Show that the uncertainty in the electric field in the ground state ($n = 0$ photons) is nonzero. (These are the vacuum fluctuations that cause spontaneous emission).

3. A Simple model of Ionic Bonding in a Sodium Chloride Molecule

Consider the NaCl molecule formed from a Cl^- and a Na^+ ion. This is an ionic system so we can assume the attractive interaction between the 2 ions is electrostatic: $-e^2/4\pi\epsilon_0r$ where r is the internuclear distance. There is also a repulsive term from the overlap of the ion cores, which we will assume to have the form $+A/r^n$ where we will have to find constants A & n .

- a) Find the minimum of $V(r) = -\frac{e^2}{4\pi\epsilon_0r} + A/r^n$, and the distance r_0 at which it occurs.
This will give the equilibrium separation r_0 for the nuclei in the NaCl molecule.
- b) Evaluate the 2nd derivative of $V(r)$ at $r = r_0$. This is the “spring constant” in the SHO approximation to the potential energy.
- c) Using the reduced mass μ (for the isotopes $m_1 = {}^{23}\text{Na}$ and $m_2 = {}^{35}\text{Cl}$), find an expression for the energy spacing of the vibrational levels in the SHO approximation. What is the lowest energy state of the vibrational motion?
- d) From diffraction experiments on NaCl molecules, we find $r_0 = 0.251$ nm. From infra-red spectroscopy, the frequency of radiation between adjacent vibrational levels is 1.14×10^{13} Hz. Use these experimental values to determine the parameters n , then A .
- e) Using the results of (a)-(d) calculate the energy (in eV) needed to dissociate an NaCl molecule from its ground state into an Na^+ and Cl^- ion.
- f) The ionization energy of the Na atom is 5.1 eV and the ionization energy of the Cl^- ion is 3.7 eV. This means that at large separations a neutral Na and Cl atom are more stable than the Na^+ and Cl^- ions. Use this and the result of (e) to find the energy required to dissociate an NaCl molecule into a Na atom and a Cl atom. Compare your result to the experimental value of 4.3 eV. Given the crude model we used, the discrepancy is not too bad.

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Q1 a)

$$[\hat{x}, \hat{p}^2] = -\hbar^2 \nabla^2 f + \hbar^2 \nabla^2 (x f) = \hbar^2 x \nabla^2 f + \hbar^2 \nabla f + \hbar^2 \nabla f - \hbar^2 x \nabla^2 f \Rightarrow 2\hbar^2 \nabla$$

$$b) [\hat{p}, \hat{x}^2] = -i\hbar \nabla x^2 f + x^2 i\hbar \nabla f = \cancel{x^2 i\hbar \nabla f} - \cancel{x^2 i\hbar \nabla f} - 2x \hbar \nabla f \Rightarrow -2x \hbar \nabla$$

$$c) [\hat{p}, \hat{H}] = -i\hbar \nabla \left(-\frac{\hbar^2}{2m} \nabla^2 f + V f \right) + \left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) (i\hbar \nabla f) = \cancel{\frac{i\hbar^3}{2m} \nabla^3 f} - \cancel{i\hbar f \nabla V} - \cancel{i\hbar \nabla V f} - \cancel{\frac{\hbar^3}{2m} \nabla^3 f} + V i\hbar \nabla f$$

$$= -i\hbar f \nabla V \Rightarrow -i\hbar [\nabla V(x)]$$

Q2 a) $\vec{B}(\vec{r}, t) = \frac{1}{2} \sqrt{\frac{2\hbar\omega_k}{L}} (\hat{a}_k e^{i(kz-\omega t)} + \hat{a}_k^\dagger e^{-i(kz-\omega t)}) \vec{e}_y,$

$$|E|^2 = c^2 |B|^2 = A^2 (\hat{a}_k e^{i\delta} + \hat{a}_k^\dagger e^{-i\delta})^2 = A^2 (\hat{a}_k e^{i\delta} + \hat{a}_k^\dagger e^{-i\delta}) (\hat{a}_k^\dagger e^{-i\delta} + \hat{a}_k e^{i\delta}) = A^2 (\hat{a}_k \hat{a}_k e^{i2\delta} + \hat{a}_k^\dagger \hat{a}_k^\dagger e^{-i2\delta} + \hat{a}_k \hat{a}_k^\dagger + \hat{a}_k^\dagger \hat{a}_k)$$

$$U = \int_0^L \frac{1}{2} \epsilon_0 A^2 (\hat{a}_k \hat{a}_k e^{i2\delta} + \hat{a}_k^\dagger \hat{a}_k^\dagger e^{-i2\delta} + \hat{a}_k \hat{a}_k^\dagger + \hat{a}_k^\dagger \hat{a}_k) dz \quad k = \frac{m\pi}{L} \quad \delta = kz - \omega t \Rightarrow \int_0^L e^{i n \delta} dz = 0$$

$$\Rightarrow U = \int_0^L \epsilon_0 A^2 (\hat{a}_k \hat{a}_k e^{i2\delta} + \hat{a}_k^\dagger \hat{a}_k^\dagger e^{-i2\delta} + \hat{a}_k \hat{a}_k^\dagger + \hat{a}_k^\dagger \hat{a}_k) dz = U = \frac{1}{2} \hbar \omega_k \epsilon_0 (\hat{a}_k \hat{a}_k^\dagger + \hat{a}_k^\dagger \hat{a}_k) = \frac{1}{2} \hbar \omega_k \epsilon_0 (2\hat{a}_k^\dagger \hat{a}_k + [\hat{a}_k, \hat{a}_k^\dagger])$$

$$b) \Rightarrow U = \frac{1}{2} \hbar \omega_k (2\hat{n} + 1) = U = \hbar \omega_k (\hat{n} + \frac{1}{2})$$

No

$$[\hat{E}, \hat{n}] = (\hat{A}_k + \hat{A}_k^\dagger) \hat{a}_k^\dagger \hat{a}_k - \hat{a}_k^\dagger \hat{a}_k (\hat{A}_k + \hat{A}_k^\dagger) = \hat{A}_k \hat{a}_k^\dagger \hat{a}_k + \hat{A}_k^\dagger \hat{a}_k^\dagger \hat{a}_k - \hat{A}_k \hat{a}_k^\dagger \hat{a}_k - \hat{A}_k^\dagger \hat{a}_k^\dagger \hat{a}_k = \hat{A}_k \hat{a}_k^\dagger \hat{a}_k + \hat{A}_k^\dagger \hat{a}_k^\dagger \hat{a}_k - \hat{A}_k \hat{a}_k^\dagger \hat{a}_k - \hat{A}_k^\dagger \hat{a}_k^\dagger \hat{a}_k = \hat{A}_k \hat{a}_k^\dagger \hat{a}_k - \hat{A}_k^\dagger \hat{a}_k^\dagger \hat{a}_k \neq 0$$

$[\hat{E}, \hat{n}] \neq 0 \Rightarrow$ No. Do not commute, so cannot observe simultaneously

c) $\vec{E} = \langle 0 | \vec{E} | 0 \rangle = \langle 0 | \hat{A}_k + \hat{A}_k^\dagger | 0 \rangle = \langle 0 | \hat{A}_k | 0 \rangle + \langle 0 | \hat{A}_k^\dagger | 0 \rangle$

$$= A \langle 0 | 1 \rangle = 0 \quad (\text{orthogonal states})$$

$$\Rightarrow \vec{E}_{\text{net}} = 0$$

d) $\sigma_E^2 = \langle (\hat{E} - \langle \hat{E} \rangle)^2 \rangle = \langle \hat{E}^2 \rangle - \langle \hat{E} \rangle^2$

$$= \langle \hat{E}^2 \rangle = A^2 \langle 1 | 1 \rangle = A^2$$

As before, in ground state $= A \cdot A \langle 1 | 1 \rangle = A^2$

$$A = \frac{1}{2} \sqrt{\frac{2\hbar\omega_k}{\epsilon_0 L}} \Rightarrow \text{In ground state, } \sigma_E^2 = \frac{\hbar\omega_k}{2\epsilon_0 L}$$

a) Starting with $\vec{E}(\vec{r}, t) = \frac{1}{2} \sqrt{\frac{2\hbar\omega_k}{L}} (\hat{a}_k e^{i(kz-\omega t)} + \hat{a}_k^\dagger e^{-i(kz-\omega t)}) \vec{e}_x,$

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Q3) a) $V(r) = -\frac{e^2}{4\pi\epsilon_0 r} + A/r^n$

$V' = \frac{e^2}{4\pi\epsilon_0 r^2} - \frac{nA}{r^{n+1}} = 0 \Rightarrow$

$r_0 = \left(\frac{4\pi\epsilon_0 n A}{e^2} \right)^{\frac{1}{n-1}}$

b) $V'' = -\frac{e^2}{2\pi\epsilon_0 r^3} + \frac{nA(n+1)}{r^{n+2}}$

$\Rightarrow k = V''(r_0) = \frac{nA(n+1)}{\left(\frac{4\pi\epsilon_0 n A}{e^2} \right)^{\frac{n+2}{n-1}}} - \frac{e^2}{2\pi\epsilon_0 \left(\frac{4\pi\epsilon_0 n A}{e^2} \right)^{\frac{3}{n-1}}}$

c) In SHO, $E_n = \hbar\omega(n + \frac{1}{2}) \Rightarrow E_0 = \hbar\omega/2$

$\omega = \sqrt{\frac{k}{\mu}}$
 $\mu = \frac{m_1 m_2}{m_1 + m_2}$

$E_0 = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}}$

k defined above

Energy spacing $= \Delta E_n = \hbar\omega = \Delta E_n = \hbar\sqrt{\frac{k}{\mu}}$

d) $r_0 = 0.251 \text{ nm}$ $\omega = 2\pi f = 2\pi \cdot 1.14 \cdot 10^{13} \Rightarrow \Delta E = \hbar f = 0.047 \text{ eV} = \hbar\omega$

$m_1 = 23 \text{ amu}$ $m_2 = 35 \text{ amu} \Rightarrow \mu = 13.88 \text{ amu}$ $2\pi \cdot 1.14 \cdot 10^{13} = \sqrt{\frac{k}{\mu}} \Rightarrow k = 118.25 \frac{\text{kg}}{\text{s}^2}$

$k = \frac{nA(n+1)}{r_0^{n+2}} - \frac{e^2}{2\pi\epsilon_0 r_0^3}$

$\frac{e^2}{2\pi\epsilon_0 r_0^3} = 182.12 \frac{\text{eV}}{\text{nm}^2}$

$118.25 \frac{\text{J}}{\text{m}^2} = 738.06 \frac{\text{eV}}{\text{nm}^2}$

$\Rightarrow \frac{nA(n+1)}{0.251 \text{ nm}^{n+2}} = 320.18 \frac{\text{eV}}{\text{nm}^2}$

$0.251 \text{ nm}^{n-1} = \frac{4\pi\epsilon_0 n A}{e^2} = 0.69446 \text{ nA} \frac{1}{\text{eV} \cdot \text{nm}}$

$\Rightarrow \frac{(n+1)r_0^{n-1}}{0.69446 \text{ nm}^{n+2}} = 320.18 = \frac{n+1}{0.69446 r_0^3} \Rightarrow n = 2.516$

$\Rightarrow A = 0.07038 \text{ eV} \cdot (\text{nm})^n$

dimensionless

e) $E_0 = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} = 0.0235 \text{ eV}$

$U_{\text{Diss}} = V(\infty) - (V(0.251 \text{ nm}) + 0.0235 \text{ eV}) =$

Dissociation Energy = 3.434 eV

f) To neutralize reduce Na^+ , oxidize $\text{Cl}^- \Rightarrow$

Cost: $3.7 - 5.1 = -1.4$

$\text{Dis}_E = V(\infty) - (-3.434 - 1.4) =$

Dissociation Energy = 4.834 eV

Fairly close to 4.6 eV ✓

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