

Physics 829: Problem Set 8

Due Wednesday, June 3, 200 at 11:59 PM

Each problem is worth 20 points.

1. In class, we discussed sp^3 hybrid orbitals constructed from the 2s and 2p states of carbon. Suppose that the wave functions of these states can be written

$$\begin{aligned}\langle \mathbf{r} | 2s \rangle &= f(r) \\ \langle \mathbf{r} | 2p_x \rangle &= g(r)x/r \\ \langle \mathbf{r} | 2p_y \rangle &= g(r)y/r \\ \langle \mathbf{r} | 2p_z \rangle &= g(r)z/r,\end{aligned}\tag{1}$$

where $f(r)$ and $g(r)$ are functions of distance from the origin only, not angular variables. Suppose also that these wave functions are normalized, so that, e. g., $\int |\langle \mathbf{r} | 2p_x \rangle|^2 d^3x = 1$, and similarly for the other three orbitals, and assume also that these functions are mutually orthogonal. Then the four sp^3 orbitals, as stated in class, are

$$\begin{aligned}|1\rangle &= \frac{1}{2}(|2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle) \\ |2\rangle &= \frac{1}{2}(|2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle) \\ |3\rangle &= \frac{1}{2}(|2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle) \\ |4\rangle &= \frac{1}{2}(|2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle)\end{aligned}\tag{2}$$

(a). Show that these four orbitals are orthonormal

(b). Show that $\langle \mathbf{r} | 1 \rangle = a(r) + b(r)(x + y + z)$, where $a(r)$ and $b(r)$ are functions of radius only, and find $a(r)$ and $b(r)$ in terms of $f(r)$ and $g(r)$. Show that the expectation value of the angular momentum operator $\mathbf{L} \cdot (\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}})/\sqrt{3}$ vanishes for this state. Hence, this orbital is said to “point” along the direction $(\hat{x} + \hat{y} + \hat{z})/\sqrt{3}$.

(c). The other three orbitals can similarly be shown to point along the directions $(-\hat{x} + \hat{y} - \hat{z})/\sqrt{3}$, $(-\hat{x} - \hat{y} + \hat{z})/\sqrt{3}$, and $(\hat{x} - \hat{y} - \hat{z})/\sqrt{3}$. Hence, show that the angle between the directions in which any two of these sp^3 orbitals point is $\cos^{-1}(-1/3) \sim 108^\circ$, as stated in class.

2. **Simple model for the diamagnetism of benzene.** As mentioned in class, benzene has a large diamagnetic susceptibility, which arises from the currents of π -bonded electrons in the benzene ring. In this problem, you will work out a highly simplified model for this diamagnetism.

Consider benzene to be a circular ring of radius R centered at the origin and perpendicular to the z axis, and assume that an electron circulating in the ring, in the absence of an applied magnetic field, has hamiltonian

$$H = \frac{p_\phi^2}{2m_e}, \quad (3)$$

where p_ϕ is the azimuthal momentum. In coordinate representation, $p_\phi = -i(\hbar/R)(d/d\phi)$.

(a). Solve the Schrödinger equation $H\Psi = E\Psi$ for this Hamiltonian. Note that Ψ depends only on ϕ . Use the relevant boundary condition to show that the allowed energies are quantized, and find the allowed energies and the corresponding wave functions.

(b). In the presence of a magnetic field perpendicular to the ring, there will be flux which penetrates the loop. In this case, the Hamiltonian becomes

$$H = \frac{1}{2m_e}(p_\phi - eA_\phi/c)^2. \quad (4)$$

If the flux through the loop is Φ , show that the vector potential can be taken to equal $\mathbf{A} = \hat{\phi}\Phi/(2\pi R)$, where $\hat{\phi}$ is a unit vector in the ϕ direction.

(c). Calculate the energy eigenvalues of the Hamiltonian in the presence of this flux. In particular, calculate the ground state energy for small flux.

(d). The induced magnetic moment is $M = -(\partial E/\partial B)$. Assume that the applied magnetic field is uniform, and calculate M . In particular, show that it is negative, corresponding to a diamagnetic susceptibility, and proportional to the loop area.

(e). The zero-field susceptibility is $(\partial M/\partial B)_{B=0}$. Calculate this quantity.

Notes: (i). Disregard the magnetic field produced by any screening currents induced by the field itself. (ii). Note that the energy levels depend only on the flux through the loop, not on the value or distribution of the magnetic field in the loop. In particular, one will get this diamagnetic response even if the magnetic field **never touches the loop**. For example, the field could be confined to the center of the loop, and yet there is a diamagnetic response arising just from the vector potential. This is known as the *Aharonov-Bohm effect*.