Physics 522 - Quantum II

Problem Set # 5 Solutions

Problem 1: Time Reversal Symmetry

For motional degrees of freedom, the time-reversal operator is defined a complex conjugation in the position basis

$$\hat{\Theta}|\psi\rangle = \hat{\Theta}\int d^3\vec{x}\; \psi(\vec{x})\,|\vec{x}\rangle \equiv \int d^3\vec{x}\; \psi^*(\vec{x})\,|\vec{x}\rangle$$

(a) An operator is said to be antiunitary if

$$\langle\tilde{\phi}|\tilde{\psi}\rangle = \langle\phi|\psi\rangle^* \quad \text{where} \quad |\tilde{\phi}\rangle = \Theta|\phi\rangle, \quad |\tilde{\psi}\rangle = \Theta|\psi\rangle$$

Now
$$|\tilde{\phi}\rangle = \int d^3\vec{x}\; \phi^*(\vec{x})\,|\vec{x}\rangle$$
$$|\tilde{\psi}\rangle = \int d^3\vec{x}\; \psi^*(\vec{x})\,|\vec{x}\rangle$$

$$\Rightarrow \langle\tilde{\phi}|\tilde{\psi}\rangle = \int d^3\vec{x}\; \phi(\vec{x})\,\psi^*(\vec{x})$$

$$= \langle\phi|\psi\rangle^*$$

✓

(b) Consider $\hat{\vec{X}}, \hat{\vec{P}}, \hat{\vec{L}}$ in position rep.

$$\Rightarrow \hat{\vec{X}}|\psi\rangle = \int d^3x \ \vec{x}\,\psi(\vec{x})\ |\vec{x}\rangle$$

$$\hat{\vec{P}}|\psi\rangle = \int d^3x \ -i\hbar\vec{\nabla}\psi(\vec{x})|\vec{x}\rangle$$

$$\hat{\vec{L}}|\psi\rangle = \int d^3x \ -i\hbar\,\vec{x}\times\vec{\nabla}\psi(\vec{x})\ |\vec{x}\rangle$$

$$\therefore\ \hat{\Theta}\hat{\vec{X}}|\psi\rangle = \int d^3x \ \vec{x}\,\psi^*(\vec{x})\ |x\rangle$$

$$= \hat{\vec{X}}\hat{\Theta}|\psi\rangle$$

$$\therefore\ \boxed{\hat{\Theta}\hat{\vec{X}}\hat{\Theta}^{-1} = \hat{\vec{X}}}$$

$$\hat{\Theta}\hat{\vec{P}}|\psi\rangle = \int d^3x \ +i\hbar\vec{\nabla}\psi^*(\vec{x})|\vec{x}\rangle = -\hat{\vec{P}}\hat{\Theta}|\psi\rangle$$

$$\Rightarrow\ \boxed{\hat{\Theta}\hat{\vec{P}}\hat{\Theta}^{-1} = -\hat{\vec{P}}}$$

$$\text{and}\ \hat{\Theta}\hat{\vec{L}}|\psi\rangle = \int d^3x \ +i\hbar\,\vec{x}\times\vec{\nabla}\psi^*(\vec{x})|\vec{x}\rangle$$

$$= -\hat{\vec{L}}\hat{\Theta}|\psi\rangle$$

$$\Rightarrow\ \boxed{\hat{\Theta}\hat{\vec{L}}\hat{\Theta}^{-1} = -\hat{\vec{L}}}$$

(c) For spin-1/2 we want to show

$\hat{\Theta} = e^{-i\frac{\pi}{\hbar}\hat{S}_y}\hat{K}_z$ is a time-reveral op.

where $(c_\uparrow|\uparrow\rangle + c_\downarrow|\downarrow\rangle)$

$= c_\uparrow^*|\uparrow\rangle + c_\downarrow^*|\downarrow\rangle$

Thus

$$\hat{K}_z\hat{\sigma}_z\hat{K}_z^{-1} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}^* = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\hat{K}_z\hat{\sigma}_x\hat{K}_z^{-1} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}^* = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\hat{K}_z\hat{\sigma}_y\hat{K}_z^{-1} = \begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix}^* = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

Now under a π rotation about the $\hat{y}$ axis

$$e^{-i\frac{\pi}{\hbar}\hat{S}_y}\hat{\sigma}_z e^{+i\frac{\pi}{\hbar}\hat{S}_y} = -\hat{\sigma}_z, \quad e^{-i\frac{\pi}{\hbar}\hat{S}_y}\hat{\sigma}_x e^{i\frac{\pi}{\hbar}\hat{S}_y} = -\hat{\sigma}_x$$

$$e^{-i\frac{\pi}{\hbar}\hat{S}_y}\hat{\sigma}_y e^{i\frac{\pi}{\hbar}\hat{S}_y} = +\hat{\sigma}_y$$

$$\therefore \hat{\Theta}\vec{S}\hat{\Theta}^{-1} = \frac{\hbar}{2}\hat{\Theta}\vec{\sigma}\hat{\Theta}^{-1} = -\vec{S}$$

$$\langle \cdot | e^{i(\alpha \hat{P}_A P_L + \beta \hat{X}_A X_L)} | \cdot \rangle$$

O_L

$$e^{i\beta \hat{X}_A \hat{X}_L} \qquad e^{i}$$

(d) The Hydrogen atom Hamiltonian

$$\hat{H} = \frac{\vec{p}^{\,2}}{2m}\left(1 - \frac{\vec{p}^{\,2}}{8m^2c^2}\right) + 2\mu_B^2 \frac{\vec{l}\cdot\vec{s}}{r^3} - \frac{e^2}{r^2}$$

relativistic correction to kinetic energy ; spin-orbit coupling

Under time-reversal symmetry
$$\begin{cases} \vec{r} \Rightarrow \vec{r} \\ \vec{p} \Rightarrow -\vec{p} \\ \vec{l} \Rightarrow -\vec{l} \\ \vec{s} \Rightarrow -\vec{s} \end{cases}$$

So $\hat{H} \Rightarrow \hat{H}$: invariant

(e) The total Hamiltonian including interactions with electromagnetic fields now includes

$$H = \frac{\left|\vec{p} + \frac{e}{c}\vec{A}\right|^2}{2m} - eV(\vec{x}) + 2\mu_B \vec{S}\cdot\vec{B}$$

where $\vec{A}$ is the vector potential
V is the scalar potential
and the last term is the Zeeman coupling to the spin.

Thus, the interaction terms

$$\hat{H}_{int} = \frac{e}{2mc}\left(\vec{p}\cdot\vec{A} + \vec{A}\cdot\vec{p}\right) - eV(\vec{x}) + 2\mu_B \vec{S}\cdot\vec{B}$$

To make the Hamiltonian ~~in~~ invariant under time reversal, we must have:

$$\Theta \vec{A} \Theta^{-1} \Rightarrow -\vec{A}$$

$$\Theta V \Theta^{-1} \Rightarrow V$$

$$\Theta \vec{B} \Theta^{-1} \Rightarrow -\vec{B}$$

since $\vec{E} = -\vec{\nabla} V$ and $\vec{B} = \vec{\nabla} \times \vec{A}$

This implies that under time reveral

$$\vec{E} \Rightarrow \vec{E}$$

$$\vec{B} \Rightarrow -\vec{B}$$

Problem 2: Gauge Symmetry

Charged particle in an electromagnetic field (static) described by potentials ($V(\vec{x})$ and $\vec{A}(\vec{x})$)

$$\hat{H} = \frac{1}{2m}\left|\hat{\vec{p}} - \frac{q}{c}\vec{A}(\hat{\vec{x}})\right|^2 + qV(\hat{\vec{x}})$$

Consider a unitary transformation $\hat{U} = e^{-i\frac{q}{\hbar c}\chi(\hat{\vec{x}})}$

$$\Rightarrow \hat{U}^\dagger \hat{H} \hat{U} = \frac{1}{2m}\left|\hat{U}^\dagger \hat{\vec{p}}\, \hat{U} - \frac{q}{c}\vec{A}(\vec{x})\right|^2 + qV(\vec{x})$$

$$\text{since } [\hat{\vec{x}}, \hat{U}] = 0$$

Aside $\hat{U}^\dagger \hat{\vec{p}}\, \hat{U} \doteq e^{+i\frac{q}{\hbar c}\chi(x)}\left(-i\hbar\vec{\nabla}\right) e^{-i\frac{q}{\hbar c}\chi(x)}$ (position rep)

$$= -\frac{q}{c}\vec{\nabla}\chi$$

$$\Rightarrow \hat{U}^\dagger \hat{H} \hat{U} = \frac{1}{2m}\left|\hat{\vec{p}} - \frac{q}{c}(\vec{A} + \vec{\nabla}\chi)\right|^2 + qV(\vec{x})$$

Thus $\hat{U}$ accomplishes the Gauge transf.

$$\vec{A} \Rightarrow \vec{A} + \vec{\nabla}\chi$$

Under this transformation $|\psi\rangle \to \hat{U}|\psi\rangle$

Thus, $\psi(x) = \langle x|\psi\rangle \longrightarrow \langle x|\hat{U}|\psi\rangle$

$$= e^{-i\phi(x)}\psi(x)$$

where $\phi(x) = \frac{q}{\hbar c}\chi(x)$

(b) Charge localized at the origin.

From classical electrodynamics we know that for a localized distribution of current and charge density we can perform a <u>multipole expansion</u>. Up to the electric dipole term the interaction energy is

$$\hat{U}_{int} = \underbrace{q V(\vec{x}_0)}_{\text{monopole}} \underbrace{- \vec{d} \cdot \vec{E}(\vec{x}_0)}_{\text{electric dipole}}$$

Where $\vec{x}_0$ = position of the distribution

this is for a particular gauge. Generally, we expand $V(\vec{x})$ and $\vec{A}(\vec{x})$ in a Taylor series about $\vec{x}_0$

$$V(\vec{x}) = V(\vec{x}_0) + (\vec{x}-\vec{x}_0) \cdot \vec{\nabla} V(\vec{x}_0)$$
$$\vec{A}(\vec{x}) = \vec{A}(\vec{x}_0) + (\text{high order terms})$$

$\leftarrow$ Contribute to mag dipole and electric quadrapole (See Jackson)

With the origin $\vec{x}_0 = \vec{0}$

$$\Rightarrow \hat{H} = \frac{1}{2m} \left| \hat{\vec{p}} - \frac{q}{c} \vec{A}(0) \right|^2 + \underbrace{q V(0)}_{\text{constant}} + q \hat{\vec{x}} \cdot \vec{\nabla} V + \cdots$$

Defining the electric dipole moment $\hat{\vec{d}} = q \hat{\vec{x}}$

$$\Rightarrow \boxed{\hat{H} = \frac{1}{2m} \left| \hat{\vec{p}} - \frac{q}{c} \vec{A}(0) \right|^2 + \hat{\vec{d}} \cdot \vec{\nabla} V + \text{const}}$$

to order electric dipole

Now perform the Gauge transformation with

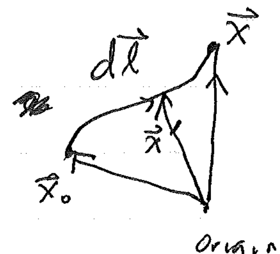
$$\chi(\vec{x}) = -\vec{x}\cdot\vec{A}(0)$$

$$\Rightarrow \vec{A} \to \vec{A} + \vec{\nabla}\chi = \vec{A} - \vec{A}(0) = 0 \quad \left(\begin{array}{c}\text{In dipole}\\ \text{approx}\end{array}\right)$$

$$\boxed{\begin{array}{l} \Rightarrow \hat{U}^{+}\hat{H}\hat{U} = \dfrac{\hat{\vec{P}}^2}{2m} - \vec{d}\cdot\vec{E}(0) + \text{constant} \\ \quad\quad \text{where} \quad \vec{E}(0) = -\vec{\nabla}V \\ \text{and now } \hat{\vec{p}} \text{ is the usual kinetic moment} \end{array}}$$

(c) Now consider the function $\xi(\vec{x}) = \frac{q}{\hbar c}\int_{\vec{x}_0}^{\vec{x}} \vec{A}(\vec{x}')\cdot d\vec{l}$

Where the integral is taken over some path connecting $\vec{x}_0$ and $\vec{x}$



Ansatz: Solution to $\hat{H}|\psi\rangle = E|\psi\rangle$

where $\hat{H}$ is $\dfrac{|\vec{p} - \frac{q}{c}\vec{A}|^2}{2m}$

has the form $\psi(x) = e^{+i\xi(x)}\psi_0(x)$

where $\hat{H}|\psi_0\rangle = E|\psi_0\rangle$ (Next Page)

Proof: Given $-\frac{\hbar^2}{2m}\nabla^2\psi_0(\vec{x}) = E\psi_0(\vec{x})$

Show $\frac{1}{2m}\left(-i\hbar\vec{\nabla} - \frac{q}{c}\vec{A}\right)^2\psi(\vec{x}) = E\psi(\vec{x})$

where $\psi(\vec{x}) = e^{i\xi(\vec{x})}\psi_0(\vec{x})$

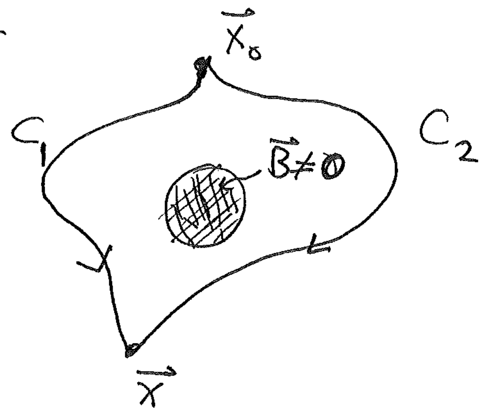
Plug in Ansatz

$$\Rightarrow \frac{e^{i\xi}}{2m}\left(-i\hbar\vec{\nabla} + \hbar\vec{\nabla}\xi - \frac{q}{c}\vec{A}\right)^2\psi_0 = E e^{i\xi}\psi_0$$

Ascale: $\vec{\nabla}\xi = \frac{q}{\hbar c}\vec{A}$

$$\Rightarrow -\frac{\hbar^2}{2m}\nabla^2\psi_0 = E\psi_0 \quad \checkmark$$

(d) The phase $\xi(\vec{x})$ depends not only on $\vec{x}$, but also the path. Consider the following geometry



Paths C_1 and C_2 both connect $\vec{x}_0$ to $\vec{x}$. Threaded between them is a "flux tube" of $\vec{B}$ field confined in a finite area.

Let $\xi_1(\vec{x}) = \int_{\vec{x}_0, C_1}^{\vec{x}} \vec{A}\cdot d\vec{l}$ $\qquad \xi_2(\vec{x}) = \int_{\vec{x}_0, C_2}^{\vec{x}} \vec{A}\cdot d\vec{l}$

$$\Rightarrow \xi_1(\vec{x}) - \xi_2(\vec{x}) = \frac{q}{\hbar c}\oint \vec{A}\cdot d\vec{l}$$ (The closed loop contour integral)

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Aside: Using Stokes' theorem

$$\oint \vec{A}\cdot d\vec{l} = \int_S (\vec{\nabla}\times\vec{A})\cdot d\vec{a} = \int_S \vec{B}\cdot d\vec{a}$$

where S is the oriented surface whose boundary is the ~~contour~~ contour (flux by right-hand-rule).

$$\Phi \equiv \int_S \vec{B}\cdot d\vec{a} \quad \text{magnetic flux}$$

$$\Rightarrow \Delta\phi_{12} = \frac{e}{\hbar c}\Phi \quad \text{(taking } q \text{ as an electron)}$$

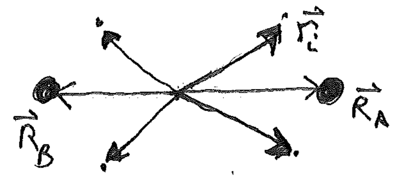
$$\therefore \boxed{\Delta\phi_{12} = \frac{1}{2\pi}\frac{\Phi}{\Phi_0}}$$

where $\Phi_0 = \frac{hc}{e} = 4.135\times10^{-7}$ Gauss cm^2 (the fundamental flux quantum)

This interference effect is known as the "Aharonov - Bohm" effect. It shows that the phase is a <u>global</u> (rather than local) property of the wave function. Even though classically, the electron would feel no force, quantum mechanically the flux tube inbetween the two possible paths effects the probability amplitude.

This effect is behind the working of a SQUID ("Superconducting Quantum Inderence Device")

Problem 3: Diatomic Molecule



Homonuclear system with clear symmetries about internuclear axis

In the Born-Oppenheimer approximation, we take the nuclei as <u>fixed</u>, providing the electrons with a static potential. The electrons also repell each other

$$\Rightarrow \hat{H} = \sum_{\substack{i \\ \text{electrons}}} \left(\frac{\hat{\vec{P}}_i^{\,2}}{2m} - \frac{Z_A e^2}{|\hat{\vec{r}}_i - \vec{R}_A|^2} - \frac{Z_B e^2}{|\hat{\vec{r}}_i - \vec{R}_B|^2} \right) + \sum_{i \neq j} \frac{e^2}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|^2}$$

For the homonuclear case considered here: $Z_A = Z_B \equiv Z_N$

<u>Symmetries</u>: Let us break up the electron coordinates into components parallel and perpendicular to the internuclear axis. Take $+z$ along R_A (though of course for the homonuclear case, this is irrelevant).

$$\vec{r}_i = \vec{x}_{\perp_i} + z_i \vec{e}_z$$

(i) A rotation about the internuclear axis transforms

$$z_i \longrightarrow z_i$$

$$\vec{x}_{\perp_i} \longrightarrow \overleftrightarrow{\mathbb{R}} \cdot \vec{x}_{\perp_i} \quad \text{(rotation matrix)}$$

$$|\overleftrightarrow{\mathbb{R}} \cdot \vec{x}_{\perp_i}|^2 = |\vec{x}_{\perp_i}|^2 \quad \left(\begin{array}{c}\text{rotation preserves} \\ \text{length}\end{array}\right)$$

Thus under this rotation

- $|\hat{\vec{r}}_i - \vec{R}_{\substack{A\\B}}|^2 = |\vec{x}_{\perp_i}|^2 + (z_i \mp R)^2$ is invariant
- $|\hat{\vec{r}}_i - \hat{\vec{r}}_j|^2 = |\vec{x}_{\perp_i} - \vec{x}_{\perp_j}|^2 + (z_i - z_j)^2$

  Again this is invariant under a rotation about $\hat{z}$ since $\overleftrightarrow{R}$ preserves lengths $\overleftrightarrow{R}\cdot\overleftrightarrow{R}^T = \overleftrightarrow{\mathbb{1}}$
- $|\vec{p}_i|^2$ is invariant since it is a scalar

$\Rightarrow$ $\boxed{\text{$\hat{H}$ is invariant under rotations about the internuclear axis (obvious by symmetry)}}$

(ii) Parity: $\vec{r}_i \to -\vec{r}_i \quad \vec{p}_i \to -\vec{p}_i$
(inversion through center of molecule)

$$\hat{H} \to \sum_i \left(\frac{\hat{\vec{p}}_i^{\,2}}{2m} - \frac{Z_A e^2}{|\hat{\vec{r}}_i + \vec{R}_A|^2} - \frac{Z_B e^2}{|\hat{\vec{r}}_i + \vec{R}_B|^2} \right) + \sum_{i\neq j} \frac{e^2}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|^2}$$

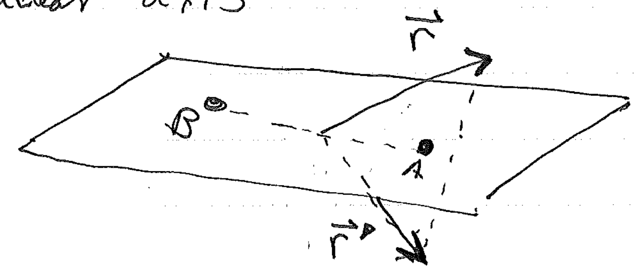
For the homonuclear case $Z_A = Z_B = Z_N$
Also $\vec{R}_A = -\vec{R}_B$

$$\text{Thus } \hat{H} \to \sum_i \left(\frac{\hat{\vec{p}}_i^{\,2}}{2m} - Z_N \left(\frac{e^2}{|\hat{\vec{r}}_i - \vec{R}_B|^2} + \frac{e^2}{|\hat{\vec{r}}_i - \vec{R}_A|^2} \right)\right) + \sum_{i\neq j} \frac{e^2}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|^2}$$
$$= \hat{H}$$

$\boxed{\text{$\hat{H}$ is invariant under parity}}$

<u>Note</u>: This is <u>not</u> true of $Z_A \neq Z_B$

(iii) Reflection through any plane containing the internuclear axis



$$\vec{r} = \vec{x}_\perp + \vec{x}_\parallel$$

$$\vec{r}' = -\vec{x}_\perp + \vec{x}_\parallel$$

- $|\hat{\vec{r}}_i - \vec{R}_{A,B}|^2 = |\hat{\vec{x}}_{\perp_i}|^2 + (\vec{x}_{\parallel_i} - \vec{R}_{A,B})^2$ is invariant
- $|\hat{\vec{r}}_i - \hat{\vec{r}}_j|^2 = |\hat{x}_{\perp_i} - \hat{x}_{\perp_j}|^2 + (\hat{x}_{\parallel i} - \hat{x}_{\parallel j})^2$ is invariant
- $|\vec{P}_i|^2$ is invariant

$\Longrightarrow$ $\boxed{\text{$\hat{H}$ is invariant under reflection through a plane containing the internuclear axis}}$

Since (i) and (ii) form a commuting set of symmetries, these energy eigenstates are specified by the eigenvalues of the respective operators.

(i) Rotation about Z, eigenvalue M (integer). However since there is no prefered positive z-direction, the energy depends only on $|M| \equiv \Lambda$

(ii) Parity eigenvalue ± 1. Denote $+1 \equiv g$ (gerade)
$-1 \equiv u$ (ungerade)

~~(iii)~~ Term notation for electron state:

$$\Lambda_g \quad \text{or} \quad \Lambda_u$$

$\Lambda = 0 \equiv \Sigma$ state, $\Lambda = 1 \equiv \Pi$ state etc.

(b) The $\hat{z}$-component of angular momentum

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

Under a reflection through the plane (Take x normal to plane) $x \to -x$, $p_x \to -p_x$ (others unchanged)

$$\Rightarrow \hat{L}_z \to -(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = -\hat{L}_z$$

Thus since $[\hat{H}, \hat{S}] = 0$ (where $\hat{S}$ = reflection oper) the states with $\hat{L}_z$ eigenvalue M and $-M$ must be <u>degenerate</u>.

Proof: Let $\hat{H}|E, M\rangle = E\,|E, M\rangle$

$$\Rightarrow \hat{H}\hat{S}|E, M\rangle = \hat{S}\hat{H}|E, M\rangle = E(\hat{S}|E, M\rangle)$$

But $\hat{S}|E, M\rangle = e^{i\phi}|E, -M\rangle$ ("symmetry breaking")
This is true even for <u>heteronuclear</u> diatomics

Thus the energy depends only on $|M| \equiv \Lambda$

~~Since~~ For $M = 0 \Rightarrow \Sigma$ states there is no degeneracy $\Rightarrow$ Σ states must be eigenstates of $\hat{S}$ with eigenvalues $+1$ or -1

reflection eigenvalue

Possible states Σ_g^+ Σ_u^+ Σ_g^- Σ_u^+

Λ eigenvalue   inversion eigenvalue

(c) Consider the Cl_2 molecule. For $|\vec{R}_A - \vec{R}_B|$ >> size of an atom ($\sim$ Å) the energy of the system should asymptote to that ~~by~~ for two free atoms.

In their ground state, each Cl atom has a total angular momentum $\ell = 1$. Thus total angular momentum magnitude can be $L = 0, 1$ or 2 with possible projections $\Lambda = 0, 1, 2$

$\Rightarrow$ Possible molecular terms

$$\boxed{\Sigma_g^{\pm},\ \Sigma_u^{\pm},\ \Pi_g,\ \Pi_u,\ \Delta_g,\ \Delta_u}$$

Note: An important symmetry we have left out of this discussion ~~is~~ is exchange. The fact that the electrons are Fermions greatly effects the spectrum. We will look at this in more detail soon.