Problem Set 3

Note: The problems labeled with a star (★) are somewhat lengthy or tricky in the derivations. You are encouraged but not obligated to solve them for extra credits.

Lecture 9

Question 1. Mathematical properties of Hermite polynomials $H_n(z)$:

$$H_n(z)=\sum_{k=0}^{\lceil n/2\rceil}\frac{(-1)^k n!}{(n-2k)!k!}(2z)^{n-2k}\text{, in which }\lceil n/2\rceil=\begin{cases} n/2 & (n\text{: even number})\\ n/2-1/2 & (n\text{: odd number})\end{cases}$$

(1) A Hermite polynomial of order n satisfies $H_n''-2zH_n'+2nH_n=0$. Prove the recursion relation: $zH_n=\frac{1}{2}H_{n+1}+nH_{n-1}$.

(2) By letting n = 0, 1, and 2, show that the $R_n(z)$ as defined in the following can also generate the Hermite polynomials $H_n(z)$

$$R_n(z)=(-1)^n\exp(z^2)\frac{d^n}{dz^n}\exp(-z^2)$$

Prove that $R_n(z)$ is equivalent to $H_n(z)$ by showing that $R_n''-2zR_n'+2nR_n=0$.

(3) Prove that the function $S(z,s)=\exp\left[z^2-(s-z)^2\right]$ can generate the Hermite polynomials, *i.e.*,

$S(z,s)=\sum_{n=0}^{+\infty}\frac{H_n(z)}{n!}s^n$, in which the Hermite polynomials $H_n(z)$ are expressed by $R_n(z)$.

★(4) Prove the orthonormalization property of the harmonic-oscillator wave functions $\psi_n(x)$ with the aid of the generating function $S(z, s)$. Find the normalization constant N_n.

$$\psi_n(x)=N_n\exp(-\frac{1}{2}z^2)H_n(z)\text{, with } z=\sqrt{\frac{m\omega}{\hbar}}x$$

(5) In problem set 2, question 6, by using the raising and lowering operators, we have shown that $x|n\rangle=\sqrt{\frac{\hbar}{2m\omega}}\left(\sqrt{n+1}|n+1\rangle+\sqrt{n}|n-1\rangle\right)$. Please use $\psi_n(x)$ to verify this relation.

Question 2. A charged diatomic molecule (ion) in an external electric field can be modeled as (within the 1D harmonic approximation): $\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 - q\varepsilon x$, in which m is the reduced mass, ω is the harmonic frequency, x is the displacement coordinate, q is the charge, and ε is the strength of the external uniform field. Solve for the exact energy levels and eigenfunctions.

Lecture 10

Question 3. (1) Start from the definition of angular momentum operator $\hat{\boldsymbol{L}} = -i\hbar\hat{\boldsymbol{r}} \times \nabla$ with the gradient operator in spherical coordinates $\nabla = \boldsymbol{e}_r \frac{\partial}{\partial r} + \boldsymbol{e}_\theta \frac{1}{r}\frac{\partial}{\partial \theta} + \boldsymbol{e}_\varphi \frac{1}{r\sin\theta}\frac{\partial}{\partial \varphi}$, prove:

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

(2) Validate $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$ with the spherical-coordinate representation.

(3) (a) Validate that the function $f(\theta,\varphi) = \sin^3\theta\cos(3\varphi)$ is an eigenfunction of $\hat{L}^2$. What is the corresponding eigenvalue?

(b) Is this function also an eigenfunction of $\hat{L}_z$?

(c) Normalize $f(\theta,\varphi)$.

Question 4. By using the spherical harmonics $|l,m\rangle$ as the basis functions, we can construct several important angular-momentum matrices. Prove the following matrix elements:

(a) $\langle l',m'|\hat{L}_z|l,m\rangle = m\hbar\delta_{ll'}\delta_{mm'}$ $\qquad$ $\langle l',m'|\hat{L}^2|l,m\rangle = l(l+1)\hbar^2\delta_{ll'}\delta_{mm'}$

(b) $\langle l',m'|\hat{L}_+|l,m\rangle = \hbar\sqrt{l(l+1)-m(m+1)}\,\delta_{ll'}\delta_{m',m+1}$

$\langle l',m'|\hat{L}_-|l,m\rangle = \hbar\sqrt{l(l+1)-m(m-1)}\,\delta_{ll'}\delta_{m',m-1}$

(c) $\langle l',m'|\hat{L}_x|l,m\rangle = \frac{\hbar}{2}\left[\sqrt{l(l+1)-m(m+1)}\,\delta_{ll'}\delta_{m',m+1} + \sqrt{l(l+1)-m(m-1)}\,\delta_{ll'}\delta_{m',m-1}\right]$

$\langle l',m'|\hat{L}_y|l,m\rangle = -\frac{i\hbar}{2}\left[\sqrt{l(l+1)-m(m+1)}\,\delta_{ll'}\delta_{m',m+1} - \sqrt{l(l+1)-m(m-1)}\,\delta_{ll'}\delta_{m',m-1}\right]$

Question 5. Consider the electronic configuration p^1d^1.

(1) Let us ignore the spin for the moment, and only consider the coupling between the orbital angular momenta $l_1 = 1$ and $l_2 = 2$. Write down all the possible coupled states $|L, M\rangle$ as linear combinations of the uncoupled states $|l_1, m_1, l_2, m_2\rangle$.

(2) Let us ignore the orbital momenta for the moment, and only consider the coupling between the spin angular momenta $s_1 = 1/2$ and $s_2 = 1/2$. Write down all the possible coupled states $|S, M_S\rangle$ as linear combinations of the uncoupled states $|s_1, m_{s1}, s_2, m_{s2}\rangle$.

(3) In the so-called *L*-*S* coupling scheme for atomic spectra, the total angular momentum *J* is obtained by coupling *L* and *S* as derived in (1) and (2), respectively.

For all the P and D terms, write down all the possible coupled states $|J, M_J\rangle$ as linear combinations of the uncoupled states $|L, M, S, M_S\rangle$. You do *not* need to write down the explicit linear combinations for the F terms. Count the number of microstates for each spectroscopic term.

Note: The spectroscopic term symbol for the coupled states $|J, M_J\rangle$ is ${}^{2S+1}L_J$, in which *L* is denoted as S, P, D, etc. $2S+1$ is called the spin multiplicity. $2J+1$ is the number of microstates, which become distinguishable under an external magnetic field (the energy levels split based on M_J).

Lecture 11

Question 6. For the electron in a hydrogenic atom (with nuclear charge +*Z*) at eigenstate $|n, l, m\rangle$:

(1) Compute the expectation value $\left\langle \frac{1}{r} \right\rangle$ by using virial theorem. (Please express all of your results in atomic units.)

(2) Compute the expectation value $\left\langle \frac{1}{r^2} \right\rangle$ by using Hellmann-Feynman theorem.

(3) What is the ratio of the centrifugal potential energy to kinetic energy?

(4) Let the radial distribution function $D_{nl}(r) = r \cdot R_{nl}(r)$, show that the radial equation becomes

$$D_{nl}'' + \left[\frac{2Z}{r} - \frac{l(l+1)}{r^2} - \left(\frac{Z}{n} \right)^2 \right] D_{nl} = 0$$

★(5) Further, by *respectively* multiplying the above radial equation by $r^{\omega} \cdot D_{nl}$ and $2r^{\omega+1} \cdot D_{nl}'$, in which $\omega > -(2l+1)$, and then integrating by part, show that

$$\frac{\omega+1}{n^2} \left\langle r^{\omega} \right\rangle - \frac{(2\omega+1)}{Z} \left\langle r^{\omega-1} \right\rangle + \frac{\omega\left[(2l+1)^2 - \omega^2 \right]}{4Z^2} \left\langle r^{\omega-2} \right\rangle = 0$$

Hint: $r \to 0$, $D(r) \sim r^{l+1}$; $r \to +\infty$, $D(r) \sim r^n e^{-Zr/n}$.

(6) Evaluate the expectation values $\left\langle r \right\rangle$ and $\left\langle r^2 \right\rangle$ by using the recursion formula derived above.

Question 7. A particle with mass m is governed by the spherical harmonic potential $V(r) = \frac{1}{2} m\omega^2 r^2$, in which ω is the angular frequency. Solve for the energy eigenvalues and eigenfunctions in Cartesian coordinates. What is the energy-level degeneracy?

Question 8. Gaussian-type basis functions are very useful for evaluating the integrals involved in practical molecular quantum mechanical calculations. We use $\boldsymbol{r}$ to represent the position of an electron, and $\boldsymbol{R}_{\mathrm{A}}$ to represent the position of a point A (which could be a nucleus or any point in space).

(1) Consider a simple 1*s*-type Gaussian function $G(a, r_{\mathrm{A}}) = \exp\left(-a r_{\mathrm{A}}^2\right)$ centered at point A, where $r_{\mathrm{A}} = \left|\boldsymbol{r}_{\mathrm{A}}\right| = \left|\boldsymbol{r} - \boldsymbol{R}_{\mathrm{A}}\right|$, and another 1*s*-type Gaussian function centered at point B, $G(b, r_{\mathrm{B}}) = \exp\left(-b r_{\mathrm{B}}^2\right)$. The two constants (parameters) a and b determine the widths of the

Gaussian functions.

Please verify that the two-center product $G(a,r_{\mathrm{A}})\cdot G(b,r_{\mathrm{B}})$ can be reduced to a single Gaussian function $G(a+b,r_{\mathrm{P}})$ centered at point P, *i.e.*, $G(a,r_{\mathrm{A}})\cdot G(b,r_{\mathrm{B}}) = K\exp\left[-(a+b)r_{\mathrm{P}}^2\right]$, in which $K=\exp\left(-\frac{ab}{a+b}\left|\boldsymbol{R}_{\mathrm{B}}-\boldsymbol{R}_{\mathrm{A}}\right|^2\right)$ and the point P is between A and B, $\boldsymbol{R}_{\mathrm{P}}=\frac{a\boldsymbol{R}_{\mathrm{A}}+b\boldsymbol{R}_{\mathrm{B}}}{a+b}$.

(2) Please show that, for the Cartesian Gaussian functions in general, the two-center product $\left[x_{\mathrm{A}}^{l}y_{\mathrm{A}}^{m}z_{\mathrm{A}}^{n}G(a,r_{\mathrm{A}})\right]\cdot\left[x_{\mathrm{B}}^{l'}y_{\mathrm{B}}^{m'}z_{\mathrm{B}}^{n'}G(b,r_{\mathrm{B}})\right]$ is equal to $\lambda KG(a+b,r_{\mathrm{P}})$, in which λ is a constant that includes the parameters l, m, n, l', m', n', and $\boldsymbol{R}_{\mathrm{A}}$, $\boldsymbol{R}_{\mathrm{B}}$, $\boldsymbol{R}_{\mathrm{P}}$. In the notation of a Cartesian Gaussian function, $\left[x_{\mathrm{A}}^{l}y_{\mathrm{A}}^{m}z_{\mathrm{A}}^{n}G(a,r_{\mathrm{A}})\right]$, r_{A} is the distance between the electron (at $\boldsymbol{r}$) and point A (at $\boldsymbol{R}_{\mathrm{A}}$), and x_{A}, y_{A}, z_{A} are the three components of $\boldsymbol{r}_{\mathrm{A}}$.

(3) Compute the 1*s*-type Gaussian function (real function) overlap integral $\left\langle G(a,r_{\mathrm{A}})\middle|G(b,r_{\mathrm{B}})\right\rangle$. This integral characterizes the overlap between the two atomic orbitals, and as you can see, the larger the separation between the nuclei A and B, the weaker the overlap.