Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 15 **Name:** ______________________

1. Show the proof of the variational principle using Dirac notation.
2. Derive the expressions for first and second order energy of perturbation theory using Dirac notation.
3. Suppose we have two eigenstates $|\psi_1\rangle$ and $|\psi_2\rangle$ that yield a different eigenvalue for a certain Hermitian operator $\hat{A}$,

$$\hat{A}\,|\psi_1\rangle = \alpha_1\,|\psi_1\rangle \qquad\qquad \hat{A}\,|\psi_2\rangle = \alpha_2\,|\psi_2\rangle$$

   Show that the eigenstates are orthonormal using bracket notation.

4. Show that if $\hat{A}$ is Hermitian, then

$$\left\langle \hat{A}\psi \middle| \hat{B}\psi \right\rangle = \left\langle \psi \middle| \hat{A}\hat{B} \middle| \psi \right\rangle .$$

5. A general state function, expressed in the form of a ket vector $|\phi\rangle$, can be written as a superpositon of the eigenstates $|1\rangle$, $|2\rangle$,... of an operator $\hat{A}$ with eigenvalues a_1, a_2,... (in other words, $\hat{A}\,|1\rangle = a_n\,|n\rangle$):

$$|\phi\rangle = c_1\,|1\rangle + c_2\,|2\rangle + ... = \sum_n c_n\,|n\rangle$$

   (a) Show that $c_n = \langle n|\phi\rangle$. This quantity is called the amplitude of measuring a_n if a measurement of $\hat{A}$ is made in the state $|\phi\rangle$.

   (b) The probability of obtaining a_n is $c_n^\star c_n$. Show that $|\phi\rangle$ can be written as $|\phi\rangle = \sum_n |n\rangle\,\langle n|\phi\rangle$.

   (c) Similarly, the corresponding bra vector of $|\phi\rangle$ can be written in terms of the corresponding bra vectors of the $|n\rangle$ as $\langle\phi| = \sum_n c_n^\star\,\langle n|$. Show that $c_n^\star = \langle\phi|n\rangle$, so that $\langle\phi| = \sum_n \langle\phi|n\rangle\,\langle n|$.

   (d) If $\langle\phi|$ is normalized, then $\langle\phi|\phi\rangle = 1$. Use this to argue that $\sum_n |n\rangle\,\langle n| = 1$ is a unit operator.