Principles of Quantum and Statistical Mechanics: True or False

1. The state function is always equal to a function of time multiplied by a function of the coordinates.
2. The state function $\psi$ can be a purely real function.
3. The state function $\psi$ can be a purely imaginary function.
4. The probability density is independent of time for a stationary state.
5. If $\hat{A}$ and $\hat{B}$ are Hermitian operators and $c_1$ and $c_2$ are real constants, then $c_1 \hat{A} + c_2 \hat{B}$ must be a Hermitian operator.
6. It is possible to measure $p^2$ (the square of the magnitude of the momentum) and the energy simultaneously to arbitrary accuracy for a particle in a box.
7. The maximum probability density for every harmonic oscillator stationary state is at the center of the potential.
8. The spherical harmonic $Y_{2,0}^0$ corresponds to a $d_z^2$ orbital.
9. The correlation energy can be calculated using a trial function which has the form of a product of single-particle wavefunctions.
10. The multiplicity of every term of an atom with an odd number of electrons must be an even number.
11. Every linear combination of solutions of the time-independent Schrödinger equation is a solution of this equation.
12. If the Hamiltonian of a system is separable, than the stationary states can be written as a product of independent eigenfunctions.
13. If the Hamiltonian of a system is separable, than the partition function can be written as a product of independent partition functions.
14. The partition function for an ideal gas of $N$ indistinguishable particles is larger than the that for the same ideal gas, but with distinguishable particles ($N>1$).
15. The thermodynamic pressure and energy can be expressed as a derivative of the logarithm of the partition function.
Match the system/quantity with the operator, eigenfunctions and eigenvalues (label the term with the letter of the system/quantity)

<table>
<thead>
<tr>
<th>System/Quantity</th>
<th>Operator</th>
<th>Eigenfunction</th>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Momentum</td>
<td>$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$</td>
<td>$R_{nl}(r)Y_l^m(\theta, \phi)$</td>
<td>$-\frac{me^4}{8\epsilon_0^2 \hbar^2 n^2}$</td>
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<tr>
<td>b) Particle in a box</td>
<td>$-\frac{\hbar^2}{2m} \nabla^2_{(x \text{ const})}$</td>
<td>$e^{ikx}$</td>
<td>$\frac{\hbar^2 l(l+1)}{2I}$</td>
</tr>
<tr>
<td>c) Harmonic Oscillator</td>
<td>$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$, $0 \leq x \leq a$</td>
<td>$Y_l^m(\theta, \phi)$</td>
<td>$\frac{n^2 \hbar^2}{8ma^2}$</td>
</tr>
<tr>
<td>d) Rigid Rotator</td>
<td>$\frac{\hbar}{i} \frac{d}{dx}$</td>
<td>$N_n H_n(\sqrt{\alpha}x)e^{-\alpha x^2}$</td>
<td>$\hbar \omega (n + \frac{1}{2})$</td>
</tr>
<tr>
<td>e) Hydrogen Atom</td>
<td>$-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$</td>
<td>$\sqrt{\frac{2}{a}} \sin(kx)$</td>
<td>$\hbar k$</td>
</tr>
</tbody>
</table>
Show your quantum savvy!

In 1971 a paper was published that applied the normalized variation function 
\[ N \exp(-br^2/a_0^2 - cr/a_0) \] to the hydrogen atom and stated that minimization of the 
variational integral with respect to the parameters \( b \) and \( c \) yielded an energy 0.7% above the 
true ground-state energy for infinite nuclear mass. Without doing any calculations, state 
why this result must be in error.

Explain why it would be incorrect to calculate the experimental ground-state energy of 
lithium by taking \( E_{2s} + 2E_{1s} \), where \( E_{2s} \) is the experimental energy needed to remove the 2s 
electron from lithium and \( E_{1s} \) is the experimental energy needed to remove the 1s electron 
from lithium.
Explain why the function $Ne^{-ar_1}e^{-ars}(r_1 - r_2)$ should not be used as a trial variation function for the helium-atom ground state. Hint: how many nodes does this trial function have?
Effect of adding a constant to the potential energy….revisited
When we discussed the particle-in-a-box, we used the free particle Hamiltonian with zero potential energy. Write an expression for this Hamiltonian, in terms of the momentum operator, as well as the standard expression involving the variable x.

In class, we claimed that using a potential energy $V=V_0$ instead of $V=0$ (still with the constraint of being inside a box situated between walls at $x=0$ and $x=a$) will not substantially alter our conclusions. Write the Schrödinger equation for this system with $V=V_0$ and find the solutions (you don’t need to write all the intermediate mathematical steps). How do the eigenfunctions depend on $V_0$? How do the eigenvalues depend on $V_0$?

Now, write a general expression for the state function $\psi(x)$ that is a linear superposition of the ground state and the 1st excited state for the above problem with $V=V_0$. Then write the corresponding expression for the time-evolution of $\psi(x)$, that is, an expression for $\Psi(x,t)$, where $\psi(x)$ is the initial condition for $\Psi(x,t)$, that is $\Psi(x,0) = \psi(x)$. How does the time-dependence of $\Psi(x,t)$ depend on $V_0$? Does this alter the probability distribution of finding it at a certain point in space $x$?
The classical ideal gas mixture...from statistical mechanics

Because the molecules in an ideal gas are independent, argue from an expression for the total system energy, that the partition function of a mixture of monatomic ideal gases is of the form:

\[ Q(N_1, N_2, V, T) = \frac{[q_1(V, T)]^{N_1}}{N_1!} \frac{[q_2(V, T)]^{N_2}}{N_2!} \]

where

\[ q_j(V, T) = \left( \frac{2\pi m_j k_B T}{\hbar^2} \right)^{3/2} V \quad j = 1, 2 \]

Show that

\[ <E> = \frac{3}{2} (N_1 + N_2) k_B T \]

and that

\[ PV = (N_1 + N_2) k_B T \]

How would \(Q\), \(<E>\) and \(P\) change if the two components were actually indistinguishable?