A

1. If Φ is a guess wave function that may or may not be normalized, H is the Hamiltonian, and E_0 is the ground-state energy, which of the following is/are *always true* as a consequence of the variational principle?

(a) $\boxed{\dfrac{\int \Phi^* H \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \geq E_0}$

(b) $\langle \Phi | H | \Phi \rangle \leq E_0$

(c) $H\Phi = E\Phi$

(d) all of the above

2. What is the Born-Oppenheimer approximation?

(a) Ignoring spin-orbit coupling in the Hamiltonian

(b) Assuming identical quantum mechanical particles to be indistinguishable from one another

(c) Assuming that spin can be included in an ad hoc fashion

(d) Assuming nuclear and electronic motions to be decoupled so that electronic energies can be computed for fixed nuclear positions

3. For a particle in a box of length 1, which of the following trial wave functions would be likely to yield the best approximation to the exact ground state wave function $\Psi_1(x) = \sqrt{2}\sin(\pi x) \quad 0 \leq x \leq 1$ (assume all functions will be normalized)

(a) $\xi(x) = x(1-x)$

(b) $\xi(x;a,b) = x^a\left(1-x^b\right)$, a and b variational parameters

(c) $\xi(x;a,b,c) = \cos^a\left(bx^c\right)$, a, b, and c variational parameters

(d) $\xi(x;a) = x^a(1-x)$, a a variational parameter

4. In atomic units, what is the Hamiltonian for the Li^+ ion (atomic number 3)?

(a) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{4}{r_{12}}$

(b) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{2}\nabla_3^2 - \frac{4}{r_1} - \frac{4}{r_2} - \frac{4}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$

(c) $\boxed{H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{4}{r_1} - \frac{4}{r_2} + \frac{1}{r_{12}}}$

(d) $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{r_{12}}$

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5. Given two gaussian functions **1** and **2** on the same nucleus defined as $\mathbf{1} = \left(\frac{2\alpha_1}{\pi}\right)^{3/4} e^{-\alpha_1 r^2}$ and $\mathbf{2} = \left(\frac{2\alpha_2}{\pi}\right)^{3/4} e^{-\alpha_2 r^2}$ with $\alpha_1 < \alpha_2$, which of the below statements is/are *true*?

(a) $\langle \mathbf{1}|T|\mathbf{1}\rangle < \langle \mathbf{2}|T|\mathbf{2}\rangle$

(b) $\left\langle \mathbf{1}\left|-\frac{1}{r}\right|\mathbf{1}\right\rangle > \left\langle \mathbf{2}\left|-\frac{1}{r}\right|\mathbf{2}\right\rangle$

(c) $< |\mathbf{1}|^2 > / < |\mathbf{2}|^2 > = 1$

(d) all of the above

6. Which of the below statements is/are *false*?

(a) Gaussian orbitals fall off in amplitude more rapidly with distance than do hydrogenic orbitals

(b) A hydrogenic orbital can be represented to arbitrary accuracy by a (possibly infinite) linear combination of gaussian orbitals

(c) Gaussian s orbitals have a maximum at the nucleus that is a cusp

(d) A hydrogenic wave function optimized as a linear combination of a finite number of guassians may not satisfy the virial theorem

7. Which of the below statements is/are *true*?

(a) Fermions have integer spin

(b) Fermion wave functions must be symmetric

(c) $\Psi = a(1)b(2) - b(1)a(2)$ is a valid fermion wave function

(d) All of the above

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8. Given

$$\alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \text{and} \quad \beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$S_x = \frac{\hbar}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \text{and} \quad S_y = \frac{\hbar}{2}\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \text{and} \quad S_z = \frac{\hbar}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

which of the below statements is/are *false*?

(a) $S_z\alpha = \frac{\hbar}{2}\alpha$

(b) $S_z\beta = \frac{\hbar}{2}\beta$

(c) $S_x\alpha = -iS_y\alpha$

(d) (b) and (c)

9. Which of the below statements about the wave function $\Psi(1,2) = \begin{vmatrix} a(1)\alpha(1) & a(1)\beta(1) \\ a(2)\alpha(2) & a(2)\beta(2) \end{vmatrix}$ is/are *false* if the spatial function a is normalized?

(a) Its normalization constant is 2

(b) It is antisymmetric to particle swapping

(c) $< \Psi \mid S^2 \mid \Psi > = 0$

(d) It is a closed-shell singlet wave function

10. A ground-state Be atom (atomic number 4) has one electron removed from its 1s orbital and another from its 2s orbital. Which of the below statements about the resulting Be^{2+} configuration is/are false?

(a) $K_{1s2s} =$ $<1s(1)2s(1) \mid 1/r_{12} \mid 1s(2)2s(2)>$

(b) The singlet state lies below the triplet state in energy

(c) The singlet-triplet splitting is $2K_{1s2s}$

(d) $J_{1s2s} =$ $<1s(1)1s(1) \mid 1/r_{12} \mid 2s(2)2s(2)>$

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Perturbation Theory and the Harmonic Oscillator

Recall that the QMHO is subject to an external potential energy of $(1/2)kx^2$ where k is the force constant. In atomic units, the first two QMHO wave functions for an oscillator having a reduced mass of 1 and a force constant of 1 are

$$\Psi_0(x) = \left(\frac{1}{\pi}\right)^{1/4} e^{-x^2/2} \qquad \Psi_1(x) = \left(\frac{4}{\pi}\right)^{1/4} xe^{-x^2/2}$$

Prove that if the quadratic potential is perturbed by a small cubic term, εx^3, where ε is a constant, the energy correction to first order in perturbation theory is zero for both of these QMHO wave functions. For Ψ_0, what is the first-order correction if the perturbing potential is quartic, i.e., εx^4?

The perturbation to the energy to first order is always $\left\langle \Psi^{(0)} \middle| V \middle| \Psi^{(0)} \right\rangle$ where $\Psi^{(0)}$ is the unperturbed wave function and V is the perturbing potential. So, in this case, the generic correction would be $\left\langle \Psi_n \middle| \varepsilon x^3 \middle| \Psi_n \right\rangle$ where n is the QMHO quantum number.

From parity, the square modulus of any QMHO wave function with itself is always even. Since the perturbing potential is odd, the argument of the integral will also be odd, and the expectation value will be zero. So, the perturbing potential εx^3 has no effect on the energy to first order.

For the perturbing potential εx^4, on the other hand, the relevant integral is even and needs to be evaluated. We have for Ψ_0

$$\begin{aligned}
\left\langle \Psi_0 \middle| \varepsilon x^4 \middle| \Psi_0 \right\rangle &= \varepsilon \left(\frac{1}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x^4 e^{-x^2} dx \\
&= 2\varepsilon \left(\frac{1}{\pi}\right)^{1/2} \frac{1 \bullet 3}{2(2)^2} \sqrt{\pi} \\
&= \frac{3\varepsilon}{4}
\end{aligned}$$

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Real vs. Complex Wave Functions

Prove that $< p_x > = 0$ for any well behaved *real* (i.e., not complex) wave function $\Psi(x)$ over the interval $-\infty \le x \le \infty$. (Hint: Use integration by parts to move your integral along and then use the properties of well behaved wave functions to finish your proof.)

Consider *any* real wave function of one dimension $\Psi(x)$.

$$\langle \Psi(x) | p_x | \Psi(x) \rangle = \int_{-\infty}^{\infty} \Psi(x)\left(-i\hbar \frac{d}{dx}\right)\Psi(x)dx$$
$$= -i\hbar \int_{-\infty}^{\infty} \Psi(x)\left(\frac{d\Psi(x)}{dx}\right)dx$$

where we have assumed without loss of generality that f is normalized over the integration interval. We can solve the integral using integration by parts. If we use

$$\int_a^b u dv = uv\Big|_a^b - \int_a^b v du$$
$$u = \Psi(x) \quad dv = \frac{d\Psi(x)}{dx}dx$$
$$du = \frac{d\Psi(x)}{dx}dx \quad v = \Psi(x)$$

then we may write

$$\int_{-\infty}^{\infty} \Psi(x)\left(\frac{d\Psi(x)}{dx}\right)dx = \left[\Psi(x)\right]^2\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \Psi(x)\left(\frac{d\Psi(x)}{dx}\right)dx$$

or

$$\int_{-\infty}^{\infty} \Psi(x)\left(\frac{d\Psi(x)}{dx}\right)dx = \frac{1}{2}\left[\Psi(x)\right]^2\Big|_{-\infty}^{\infty}$$

but, we know that a well-behaved wave function must go to zero at its integration endpoints, so the r.h.s. of the final equation is just 0. Thus, *any real wave function* has an expectation value of 0 for the momentum operator. We can think of this result as deriving from a superposition of left- and right-moving particle wave functions.

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