Quantum Computing for Quantum Chemistry - Exercises

## EUMEN Team - Quantinuum

November 21, 2022

1 Lecture 1

1. Considering the energy levels of atomic orbitals in each valence shell shown in figure 1, and using a periodic table:

   (a) Write the electron configurations for the following atoms and ions:

      i Ne,

      ii Ar^{+},

      iii C,

      iv O,

      v (optional) Br^{-}.

      Hint: For Mg, the electron configuration is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2$, or $1s^2 2s^2 2p^6 3s^2$ since the p shell is fully occupied. Aufbau principle dictates that the lowest energy atomic orbitals are filled first.
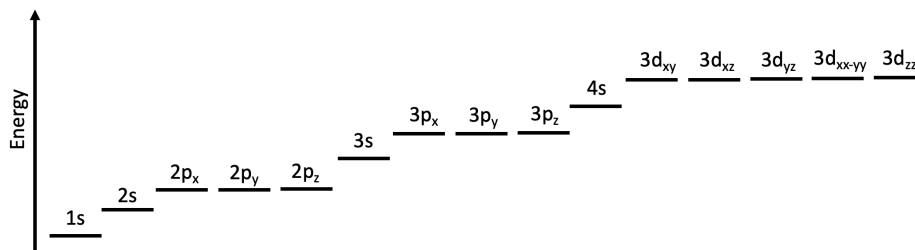
Figure 1: Atomic orbital energy levels.

   (b) For the following systems, construct molecular orbital diagrams:

      i. Hydrogen Fluoride (HF)

      ii. (optional) Water (H_2O)

      Hint: Not all molecular orbitals are bonding orbitals! The heavier an atom, the lower the energy of the core electrons, so they are often

bystanders in bonding interactions. The number of molecular orbitals must be equal to the number of atomic orbitals. For part (ii) first think about how you can combine the two H $1s$ orbitals, and place those combinations on one side of your MO diagram.

(c) The ground-state wavefunction of the Hydrogen atom is given by,

$$\psi_{1,0,0} = \left(\frac{\xi^3}{\pi}\right)^{\frac{1}{2}} e^{-\xi r}. \tag{1}$$

Since this is an isolated, one-electron system, we only need to consider electronic kinetic energy and nucleus-electron attraction. The kinetic energy operator is the radial Laplacian,

$$\hat{T} = -\frac{1}{2r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right). \tag{2}$$

The potential energy operator for a hydrogen-like system is,

$$\hat{V} = -\frac{Z}{r}. \tag{3}$$

The expectation values of each operator $\hat{T}$ and $\hat{V}$ with respect to ψ are given by

$$\langle \hat{T} \rangle = \frac{\xi^2}{2m} \tag{4}$$

and

$$\langle \hat{V} \rangle = -\xi Z, \tag{5}$$

respectively, where m is the electron mass and Z is the charge of the nucleus. The total energy is,

$$E = \frac{\xi^2}{2m} - \xi Z. \tag{6}$$

For the **Hydrogen atom**:

 i. Use this information to find the optimum value of ξ. That is, the value which gives the lowest total energy.

 Hint: In atomic units $m = 1$ and $Z = 1$. Full description in Szabo & Ostlund (chapter 2).

 ii. Plot the kinetic, potential and total energies as functions of ξ on the same graph.

 iii. (optional) Add to your plot from (ii), one side of the virial equation $(-V/2)$. Where does this intersect with the kinetic energy? Is this consistent with the value determined for ξ in part (i) of this question?

iv. Inspect figure 2 and, with the information from part (ii) of this question, arrive at your own conclusions for the origin of the bond in H_2^+. How is the molecular orbital expanding and contracting throughout the formation of the bond?

Hint: Begin at large internuclear separation, the bond is at its strongest at $2a_0$.
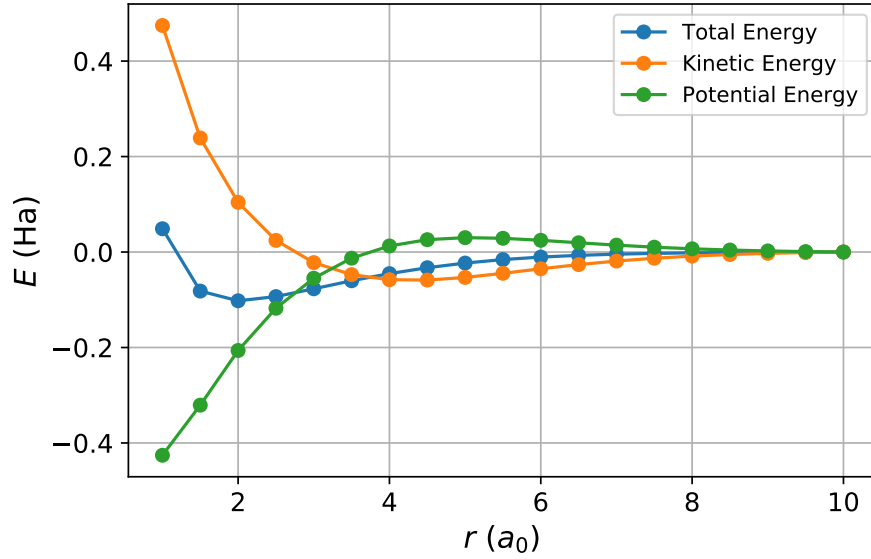
Figure 2: The total (blue line), kinetic (orange line) and potential (green line) energy against nuclear separation for H_2^+, minus the asymptotic values.

2. Given that the 2s $(2, 0, 0)$ hydrogen atom solution is described by

$$\psi_{2,0,0} = \frac{1}{4\sqrt{2\pi}a_0^{3/2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}. \tag{7}$$

Using the Born rule $|\langle \psi(r)|\psi(r)\rangle|^2 = \rho(r)$ for probability denisty, with sympy.plotting draw the radial distribution functions for the 1s and 2s solutions.

3. For the Shrodinger equation governing the particle in a box. For the general solution

$$\psi(x) = C\sin(kx) + D\cos(kx) \tag{8}$$

and the boundary conditions

$$\psi(0) = 0 = C\sin(0) + D\cos(0) = D \tag{9}$$

and $D = 0$. At $x = L$,

$$\psi(L) = 0 = C\sin(kL) \tag{10}$$

show that the energy is quantized by

$$E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2} = \frac{n^2 h^2}{8mL^2} \tag{11}$$

4. The general solution to the Hydrogen atom is given by:

$$\psi_{n\ell m}(r,\theta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}}\, e^{-r/na_0} \left(\frac{2r}{na_0}\right)^\ell L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0}\right)\cdot Y_\ell^m(\theta,\varphi) \tag{12}$$

where $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_q q^2}$ is the Bohr radius, $L_{n-\ell-1}^{2\ell+1}(\cdots)$ are the generalized Laguerre polynomials of degree $n-\ell-1$ given by

$$L_n^{(\alpha)}(x) = \frac{x^{-\alpha}e^x}{n!}\frac{d^n}{dx^n}\left(e^{-x}x^{n+\alpha}\right) = \frac{x^{-\alpha}}{n!}\left(\frac{d}{dx}-1\right)^n x^{n+\alpha}. \tag{13}$$

$Y_\ell^m(\theta,\varphi)$ are the spherical harmonics given by

$$Y_\ell^m(\theta,\varphi) = (-1)^m \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\, P_\ell^m(\cos\theta)\, e^{im\varphi} \tag{14}$$

n,ℓ,m are the principal quantum number, azimuthal quantum number, and magnetic quantum number, respectively, which take the values $n = 1,2,3,\ldots$, $\ell = 0,1,2,\ldots,n-1$, $m = -\ell,\ldots,\ell$.

(a) Using numpy or sympy (or both), plot all the f orbitals in at a suitable radius using the born rule $|\langle\psi(r)|\psi(r)\rangle|^2 = \rho(r)$. Where the edge of the isosphere is some arbitrary probability density.

Hint: https://www.cfm.brown.edu/people/dobrush/am33/SymPy/part1.html or https://matplotlib.org/stable/gallery/mplot3d/surface3d_radial.html

(b) Plot a g orbital, why has this not been observed in matter.

(c) Where would an atom with a g valence electron go in the periodic table.

5. Using the linear combination of unitaries. Find the energy of the bonding and anitbonding orbital in H2 a $1s$ - $1s$ σ bond. Where the energy is given by the secular equation. (This can be done by hand or on a computer.)

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}\begin{pmatrix} c_A \\ c_B \end{pmatrix} = E\begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix}\begin{pmatrix} c_A \\ c_B \end{pmatrix} \tag{15}$$

With the Hamiltonian elements given by:

$$H_{AA} = \int d\mathbf{r} s_A^*(\mathbf{r}) H_{LCAO} s_A(\mathbf{r})$$

$$= \int d\mathbf{r} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \left[\nabla_A^2 + \frac{1}{|r - R_A|} + \frac{1}{|r - R_B|} \right] \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \tag{16}$$

and the overlap elements

$$S_{AA} = \int d\mathbf{r} s_A^*(\mathbf{r}) s_A(\mathbf{r})$$

$$= \int d\mathbf{r} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \frac{1}{\pi} \sqrt{\frac{1}{a_0}} e^{-\frac{r}{a_0}} \tag{17}$$