2. Atoms

Mar. 5, 2020

Wave functions of hydrogen

$$\frac{-\hbar^2}{2m}\nabla^2\Psi - \frac{Ze^2}{4\pi\varepsilon_0 r}\Psi = E\Psi$$

Solve with the boundary condition $\Psi \to 0 \quad \text{as} \quad \left|\vec{r}\right| \to \infty$

Assume $\Psi(r,\theta,\varphi) = R(r)\Theta(\theta)\Phi(\varphi)$

Atomic orbitals

$$\phi^Z_{1s} = \sqrt{\frac{Z^3}{\pi a_0^3}}\, e^{-\frac{Zr}{a_0}},$$

$$\phi^Z_{2s} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}}\left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}},$$

$$\phi^Z_{2px} = \frac{1}{8}\sqrt{\frac{Z^3}{\pi a_0^3}}\,\frac{Zr}{a_0}\, e^{-\frac{Zr}{2a_0}}\,\sin\theta\cos\varphi,$$

$$\phi^Z_{2py} = \frac{1}{8}\sqrt{\frac{Z^3}{\pi a_0^3}}\,\frac{Zr}{a_0}\, e^{-\frac{Zr}{2a_0}}\,\sin\theta\sin\varphi,$$

$$\phi^Z_{2pz} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}}\,\frac{Zr}{a_0}\, e^{-\frac{Zr}{2a_0}}\,\cos\theta,$$

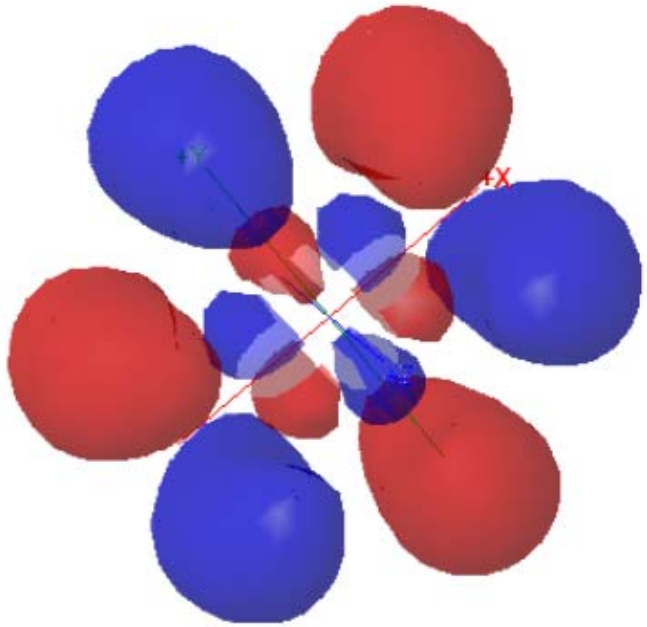
Z is the number of protons

$$E = -\frac{Z^2 m e^4}{32\pi^2\epsilon_0^2\hbar^2 n^2} = -\frac{13.6 Z^2}{n^2}\ \text{eV}.$$

Atomic orbitals

http://lampx.tugraz.at/~hadley/ss1/molecules/atoms/AOs.php

5f



Atomic orbitals:

1s								
2s						2px	2py	2pz
3s						3px	3py	3pz
4s	3d xy	3d yz	3d xz	3d z²	3d x²-y²	4px	4py	4pz
5s	4d xy	4d yz	4d xz	4d z²	4d x²-y²	5px	5py	5pz
6s	5d xy	5d yz	5d xz	5d z²	5d x²-y²	6px	6py	6pz

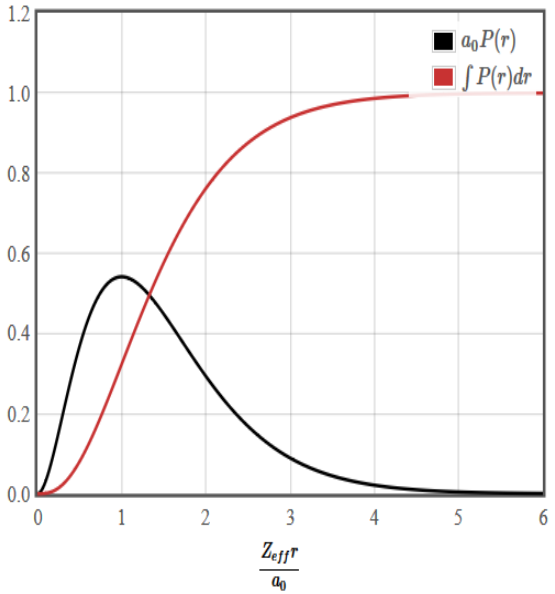
4f	4f	4f	4f	4f	4f	4f
5f	5f	5f	5f	5f	5f	5f

$$\langle \phi_m | H | \phi_n \rangle = \frac{-\hbar^2}{2m} \langle \phi_m | \nabla^2 | \phi_n \rangle - \frac{2e^2}{4\pi\varepsilon_0} \langle \phi_m | \frac{1}{|\vec{r}|} | \phi_n \rangle$$

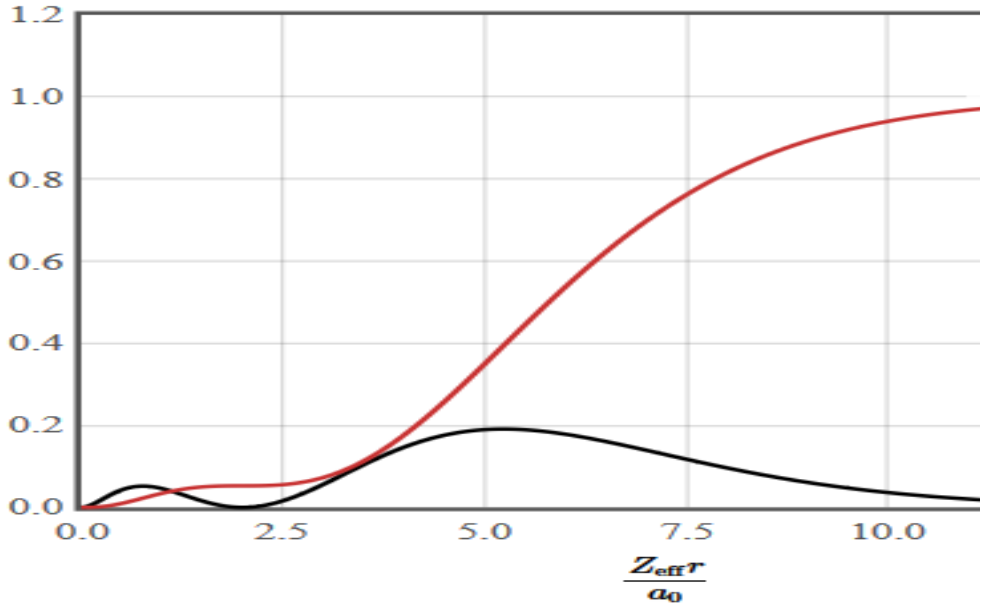
Radial distribution function

$$P(r) = 4\pi r^2 |\Psi(r)|^2 dr$$

$$\phi_{1s}^{Z} = \sqrt{\frac{Z^3}{\pi a_0^3}} \exp\left(-\frac{Zr}{a_0}\right)$$



$$\phi_{2s}^{Z} = \frac{1}{4}\sqrt{\frac{Z^3}{2\pi a_0^3}} \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$$



Expectation energy

Often in molecular or solid state physics we know the Hamiltonian but we can't solve the Schrödinger equation associated with this Hamiltonian. In these cases we often guess a solution and then calculate the corresponding energy.

Consider the Hamiltonian for a hydrogen atom. In spherical coordinates it is,

$$H\psi = \frac{-\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right] - \frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi.$$

Find the expectation value of the energy $E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}$ for the following wavefunction,

$$\psi = \exp\left(\frac{-r^2}{a^2}\right),$$

where a is a parameter. Note that this wavefunction is not an eigenfunction of the Hamiltonian. Determine the value of a that minimizes the energy. Compare a to the Bohr radius $a_0 = 5.3 \times 10^{-11}$ m.

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\iiint \Psi^*(r,\theta,\varphi)H\Psi(r,\theta,\varphi)r^2\sin\theta dr d\theta d\varphi}{\iiint \Psi^*(r,\theta,\varphi)\Psi(r,\theta,\varphi)r^2\sin\theta dr d\theta d\varphi}$$

Helium atom

$$\frac{-\hbar^2}{2m}\left(\nabla_1^2\Psi+\nabla_2^2\Psi\right)-\frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_1\right|}\Psi-\frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_2\right|}\Psi+\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_1-\vec{r}_2\right|}\Psi=E\Psi$$

$\left|\Psi\left(\vec{r}_1,\vec{r}_2\right)\right|^2$ is the probability to find one of the electrons at r_1 and the other one at r_2.

Helium atom

neglect the electron-electron interaction term

$$H_{red}^{He} = \frac{-\hbar^2}{2m}\left(\nabla_1^2\Psi + \nabla_2^2\Psi\right) - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_1\right|}\Psi - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_2\right|}\Psi + \cancel{\frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_1 - \vec{r}_2\right|}\Psi} = E\Psi$$

assume a product wave function

$$\Psi\left(\vec{r}_1, \vec{r}_2\right) = \phi_1\left(\vec{r}_1\right)\phi_2\left(\vec{r}_2\right)$$

Separation of variables (Trennung der Veränderlichen)

$$\frac{-\hbar^2}{2m}\nabla_1^2\phi_1\phi_2 - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_1\right|}\phi_1\phi_2 = \frac{\hbar^2}{2m}\nabla_2^2\phi_1\phi_2 + \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_2\right|}\phi_1\phi_2 + E\phi_1\phi_2$$

divide by $\phi_1\phi_2$

$$\frac{-\hbar^2}{2m\phi_1}\nabla_1^2\phi_1 - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_1\right|} = C = \frac{\hbar^2}{2m\phi_2}\nabla_2^2\phi_2 + \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_2\right|} + E$$

$$\frac{-\hbar^2}{2m}\nabla_1^2\phi_1 - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_1\right|}\phi_1 = C\phi_1 \qquad \frac{-\hbar^2}{2m}\nabla_2^2\phi_2 - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_2\right|}\phi_2 = \left(E - C\right)\phi_2$$

Indistinguishable particles

$$\left|\Psi(\vec{r}_1,\vec{r}_2)\right|^2 = \left|\Psi(\vec{r}_2,\vec{r}_1)\right|^2$$

$$\Psi(\vec{r}_1,\vec{r}_2) = \pm\Psi(\vec{r}_2,\vec{r}_1)$$

bosons $\Psi(\vec{r}_1,\vec{r}_2) = \Psi(\vec{r}_2,\vec{r}_1)$ integer spin: photons, phonons, ^{4}He

fermions $\Psi(\vec{r}_1,\vec{r}_2) = -\Psi(\vec{r}_2,\vec{r}_1)$ half integer spin: electrons, neutrons, protons, ^{3}He

Spin

Spin appears naturally in the relativistic formulation of quantum mechanics but in the nonrelativistic formulation, we just add the spins states.

$\uparrow$ = spin up
$\downarrow$ = spin down

Spin orbitals: $\phi_{1s}\uparrow, \phi_{1s}\downarrow, \phi_{2s}\uparrow, \phi_{2s}\downarrow, \cdots$

Slater determinants

The antisymmetric *N* electron wave function can be written,

$$\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_{1s}\uparrow(\vec{r}_1) & \phi_{1s}\downarrow(\vec{r}_1) & \cdots & \phi_N\uparrow(\vec{r}_1)\\ \phi_{1s}\uparrow(\vec{r}_2) & \phi_{1s}\downarrow(\vec{r}_2) & \cdots & \phi_N\uparrow(\vec{r}_2)\\ \vdots & \vdots & & \vdots\\ \phi_{1s}\uparrow(\vec{r}_N) & \phi_{1s}\downarrow(\vec{r}_N) & \cdots & \phi_N\uparrow(\vec{r}_N)\end{vmatrix}.$$

Exchanging two rows changes the sign of the determinant.

If two columns are the same, the determinant is zero = Pauli exclusion.

Dirac notation: $\Psi(\vec{r}_1,\vec{r}_2,\cdots,\vec{r}_N)=|\phi_{1s}\uparrow,\phi_{1s}\downarrow,\cdots,\phi_N\uparrow\rangle$

Helium ground state

$$H_{total} = \frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0 \left|\vec{r}_1\right|} - \frac{2e^2}{4\pi\varepsilon_0 \left|\vec{r}_2\right|} + \frac{e^2}{4\pi\varepsilon_0 \left|\vec{r}_1 - \vec{r}_2\right|}$$

Approximate antisymmetrized wave function (neglecting electron-electron interactions)

$$\Psi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{He}(\vec{r}_1)\uparrow & \phi_{1s}^{He}(\vec{r}_1)\downarrow \\ \phi_{1s}^{He}(\vec{r}_2)\uparrow & \phi_{1s}^{He}(\vec{r}_2)\downarrow \end{vmatrix} = \frac{\phi_{1s}^{He}(\vec{r}_1)\phi_{1s}^{He}(\vec{r}_2)}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right)$$

Energy neglecting *e*-*e* interactions $\longrightarrow$ $E = 2 \times \frac{-13.6Z^2}{n^2} = -108.8 \text{ eV}$

Approximate ground state evaluated with the total Hamiltonian $\longrightarrow$ $E = \frac{\langle \Psi | H_{total} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = -74.83 \text{ eV}$

Matrix elements

$$E_0^{\mathrm{He}} \approx \frac{\langle \Psi_0^{\mathrm{He}} | H_{\mathrm{total}}^{\mathrm{He}} | \Psi_0^{\mathrm{He}} \rangle}{\langle \Psi_0^{\mathrm{He}} | \Psi_0^{\mathrm{He}} \rangle}$$

$$\frac{\iiint \iiint \Psi^*(x_1, y_1, z_1, x_2, y_2, z_2) H \Psi(x_1, y_1, z_1, x_2, y_2, z_2) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2}{\iiint \iiint \Psi^*(x_1, y_1, z_1, x_2, y_2, z_2) \Psi(x_1, y_1, z_1, x_2, y_2, z_2) dx_1 dy_1 dz_1 dx_2 dy_2 dz_2}$$

Helium ground state

Try other wave functions in the full Hamiltonian

$$H_{total} = \frac{-\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_1\right|} - \frac{2e^2}{4\pi\varepsilon_0\left|\vec{r}_2\right|} + \frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_1 - \vec{r}_2\right|}$$

$$\Psi(\vec{r}_1, \vec{r}_2) = \exp\left(\frac{-\alpha r_1}{a_0}\right)\exp\left(\frac{-\alpha r_2}{a_0}\right) \times \left(\text{polynomial in } r_1 \text{ and } r_2\right)$$

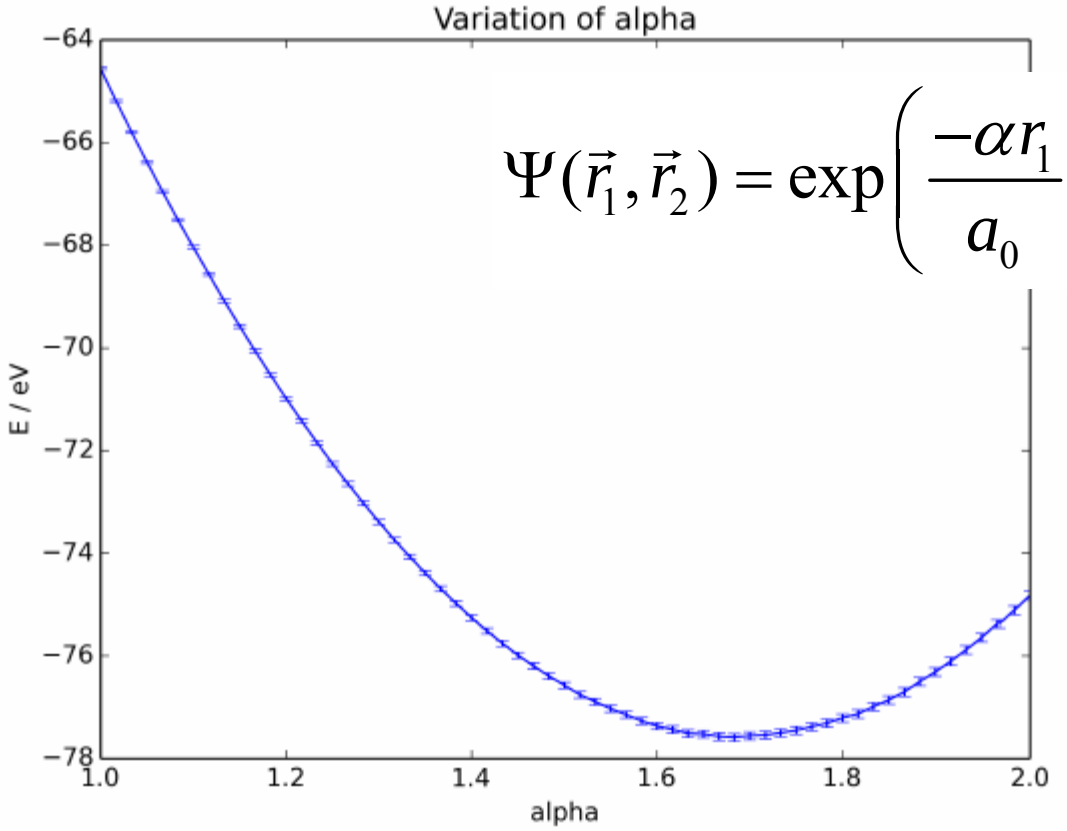
Electron screening makes the wave function larger

$$E = \frac{\left\langle \Psi \middle| H_{total} \middle| \Psi \right\rangle}{\left\langle \Psi \middle| \Psi \right\rangle}$$

4.1 Helium

The results of the total energy of the helium ground state for different effective nuclear charges α are plotted in 1. The minimum (and therfore best estimate) lies at

$$\begin{aligned} \alpha &= (1.685 \pm 0.005) \\ E &= (-77.50 \pm 0.03)\, eV \end{aligned} \tag{14}$$



$$\Psi(\vec{r}_1, \vec{r}_2) = \exp\left(\frac{-\alpha r_1}{a_0}\right)\exp\left(\frac{-\alpha r_2}{a_0}\right)$$

Student project Michael Scherbela, 2014

Slater's rules

Effective Nuclear Charge Z_{eff}

	1s	2s,2p
H	1	
He	1.7	
Li	2.7	1.3
Be	3.7	1.95
B	4.7	2.6
C	5.7	3.25
N	6.7	3.9
O	7.7	4.55
Cl	8.7	5.2
Ne	9.7	5.85

Slater, J. C., Atomic Shielding Constants, Phys. Rev. 36, pp. 57–64, 1930. doi:10.1103/PhysRev.36.57

Helium ground state

$e^{-2r_1}e^{-2r_2}$	-74.83 eV
$e^{-\alpha r_1}e^{-\alpha r_2}$	-77.4885 eV
$e^{-\alpha(r_1+r_2)}(1+c\lvert\vec{r}_1-\vec{r}_2\rvert)$	-78.6714 eV
1078 parameters	-79.0142 eV

The true wave function cannot be written as a product of two one-electron wave functions.

Helium excited states

One electron in 1s and one in 2s, $\uparrow\uparrow, \downarrow\downarrow, \downarrow\uparrow$, and $\uparrow\downarrow$

$$\Psi_I = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\mathrm{He}} \uparrow (\vec{r}_1) & \phi_{2s}^{\mathrm{He}} \uparrow (\vec{r}_1) \\ \phi_{1s}^{\mathrm{He}} \uparrow (\vec{r}_2) & \phi_{2s}^{\mathrm{He}} \uparrow (\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\phi_{2s}^{\mathrm{He}}(\vec{r}_2) - \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\right) \uparrow\uparrow,$$

$$\Psi_{II} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\mathrm{He}} \downarrow (\vec{r}_1) & \phi_{2s}^{\mathrm{He}} \downarrow (\vec{r}_1) \\ \phi_{1s}^{\mathrm{He}} \downarrow (\vec{r}_2) & \phi_{2s}^{\mathrm{He}} \downarrow (\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\phi_{2s}^{\mathrm{He}}(\vec{r}_2) - \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\right) \downarrow\downarrow,$$

$$\Psi_{III} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\mathrm{He}} \uparrow (\vec{r}_1) & \phi_{2s}^{\mathrm{He}} \downarrow (\vec{r}_1) \\ \phi_{1s}^{\mathrm{He}} \uparrow (\vec{r}_2) & \phi_{2s}^{\mathrm{He}} \downarrow (\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1) \uparrow \phi_{2s}^{\mathrm{He}}(\vec{r}_2) \downarrow - \phi_{2s}^{\mathrm{He}}(\vec{r}_1) \downarrow \phi_{1s}^{\mathrm{He}}(\vec{r}_2) \uparrow\right),$$

$$\Psi_{IV} = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_{1s}^{\mathrm{He}} \downarrow (\vec{r}_1) & \phi_{2s}^{\mathrm{He}} \uparrow (\vec{r}_1) \\ \phi_{1s}^{\mathrm{He}} \downarrow (\vec{r}_2) & \phi_{2s}^{\mathrm{He}} \uparrow (\vec{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1) \downarrow \phi_{2s}^{\mathrm{He}}(\vec{r}_2) \uparrow - \phi_{2s}^{\mathrm{He}}(\vec{r}_1) \uparrow \phi_{1s}^{\mathrm{He}}(\vec{r}_2) \downarrow\right).$$

$$E = \frac{\langle \Psi | H_{red}^{He} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = -\frac{13.6 * 2^2}{1^2} - \frac{13.6 * 2^2}{2^2} = -68 \text{ eV}$$

The antisymmetric solution $\Psi = 0$ for $\vec{r}_1 = \vec{r}_2$.

Transform to symmetric and antisymmetric orbital solutions

$$\Psi_I = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\phi_{2s}^{\mathrm{He}}(\vec{r}_2) - \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\right)\uparrow\uparrow,$$

$$\Psi_{II} = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\phi_{2s}^{\mathrm{He}}(\vec{r}_2) - \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\right)\downarrow\downarrow,$$

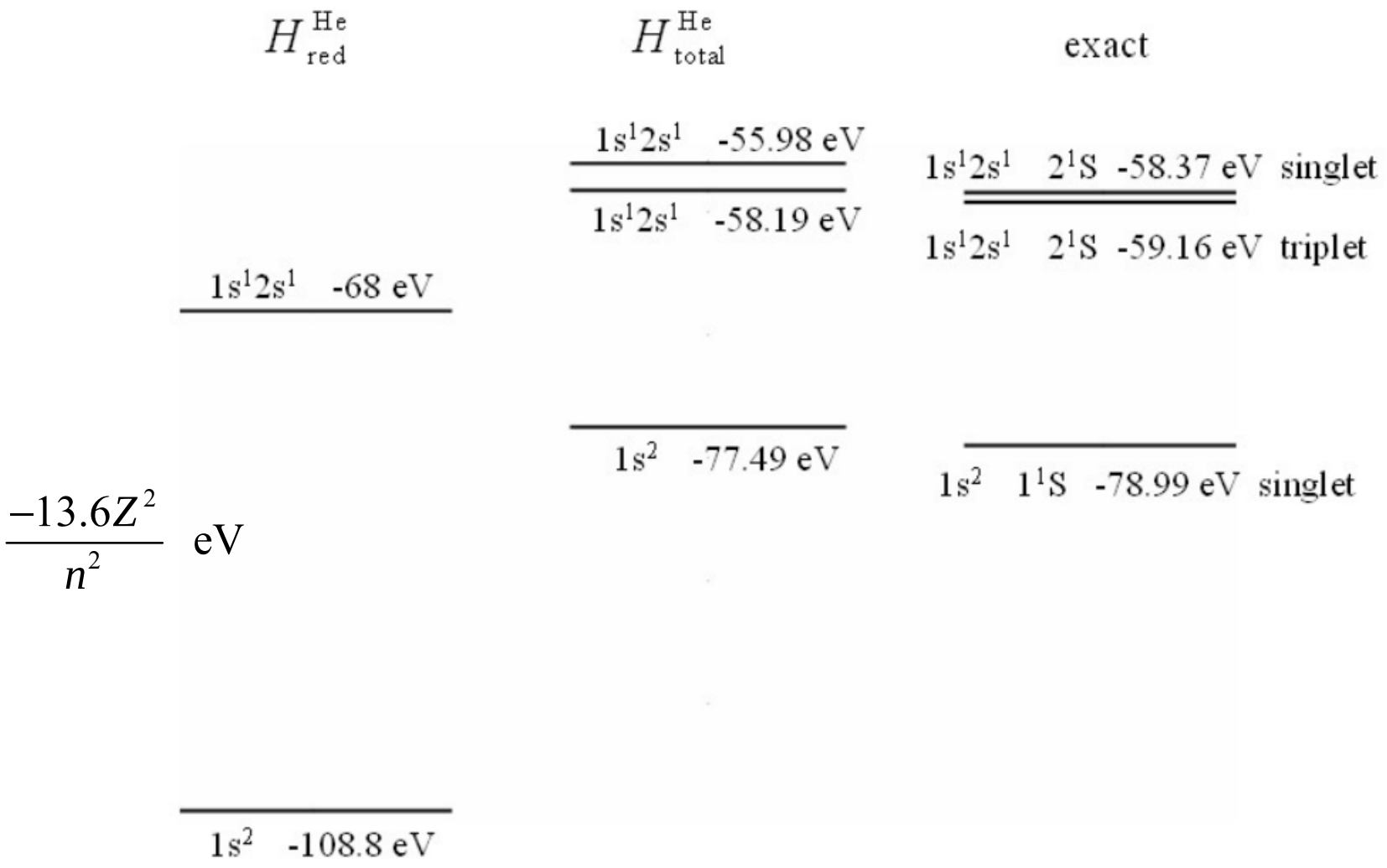
$$\Psi_{III} = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\uparrow\phi_{2s}^{\mathrm{He}}(\vec{r}_2)\downarrow - \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\downarrow\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\uparrow\right),$$

$$\Psi_{IV} = \frac{1}{\sqrt{2}}\left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\downarrow\phi_{2s}^{\mathrm{He}}(\vec{r}_2)\uparrow - \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\uparrow\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\downarrow\right).$$

$$\Psi_V = \frac{1}{\sqrt{2}}\left(\Psi_{III} + \Psi_{IV}\right) = \frac{1}{2}\left(\left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\phi_{2s}^{\mathrm{He}}(\vec{r}_2) - \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\right)(\uparrow\downarrow + \downarrow\uparrow)\right),$$

$$\Psi_{VI} = \frac{1}{\sqrt{2}}\left(\Psi_{III} - \Psi_{IV}\right) = \frac{1}{2}\left(\left(\phi_{1s}^{\mathrm{He}}(\vec{r}_1)\phi_{2s}^{\mathrm{He}}(\vec{r}_2) + \phi_{2s}^{\mathrm{He}}(\vec{r}_1)\phi_{1s}^{\mathrm{He}}(\vec{r}_2)\right)(\uparrow\downarrow - \downarrow\uparrow)\right).$$

Helium excited states



NIST National Institute of Standards and Technology Physics Laboratory

Basic Atomic Spectroscopic Data

Main Page | Finding List | Element Name | Atomic Number | Periodic Table

Switch to ASCII Version

Select an element to access data

^{1}H																	^{2}He
^{3}Li	^{4}Be											^{5}B	^{6}C	^{7}N	^{8}O	^{9}F	^{10}Ne
^{11}Na	^{12}Mg											^{13}Al	^{14}Si	^{15}P	^{16}S	^{17}Cl	^{18}Ar
^{19}K	^{20}Ca	^{21}Sc	^{22}Ti	^{23}V	^{24}Cr	^{25}Mn	^{26}Fe	^{27}Co	^{28}Ni	^{29}Cu	^{30}Zn	^{31}Ga	^{32}Ge	^{33}As	^{34}Se	^{35}Br	^{36}Kr
^{37}Rb	^{38}Sr	^{39}Y	^{40}Zr	^{41}Nb	^{42}Mo	^{43}Tc	^{44}Ru	^{45}Rh	^{46}Pd	^{47}Ag	^{48}Cd	^{49}In	^{50}Sn	^{51}Sb	^{52}Te	^{53}I	^{54}Xe
^{55}Cs	^{56}Ba	*	^{72}Hf	^{73}Ta	^{74}W	^{75}Re	^{76}Os	^{77}Ir	^{78}Pt	^{79}Au	^{80}Hg	^{81}Tl	^{82}Pb	^{83}Bi	^{84}Po	^{85}At	^{86}Rn
^{87}Fr	^{88}Ra	+															
* Lanthanides			^{57}La	^{58}Ce	^{59}Pr	^{60}Nd	^{61}Pm	^{62}Sm	^{63}Eu	^{64}Gd	^{65}Tb	^{66}Dy	^{67}Ho	^{68}Er	^{69}Tm	^{70}Yb	^{71}Lu
+ Actinides			^{89}Ac	^{90}Th	^{91}Pa	^{92}U	^{93}Np	^{94}Pu	^{95}Am	^{96}Cm	^{97}Bk	^{98}Cf	^{99}Es				

$$E = hf = hc/\lambda$$

Names refer to approximate solutions

http://physics.nist.gov/PhysRefData/Handbook/Tables/heliumtable5.htm

Energy Levels of Neutral Helium (He I)

Configuration	Term	J	Level(cm^{-1})	Ref.
$1s^2$	^{1}S	0	0.000	M02
1s2s	^{3}S	1	159855.9745	M02
1s2s	^{1}S	0	166277.4403	M02
1s2p	^{3}P°	2	169086.7666	M02
		1	169086.8430	M02
		0	169087.8309	M02
1s2p	^{1}P°	1	171134.8970	M02
1s3s	^{3}S	1	183236.7918	M02
1s3s	^{1}S	0	184864.8294	M02
1s3p	^{3}P°	2	185564.5620	M02
		1	185564.5840	M02
		0	185564.8547	M02
1s3d	^{3}D	3	186101.5463	M02
		2	186101.5488	M02
		1	186101.5930	M02
1s3d	^{1}D	2	186104.9668	M02
1s3p	^{1}P°	1	186209.3651	M02
1s4p	^{1}P°	1	191492.7120	M02
He II (^{2}S$_{1/2}$)	***Limit***		**198310.6691**	M02