Expressions useful for discussion of Helium Description

$$H = T_1 \ + \ V_1 \ + \ T_2 \ + \ V_2 \ + V_{12}$$

$$H = T_1(\mathbf{r}_1) \ + \ V_1(\mathbf{r}_1) \ + \ T_2(\mathbf{r}_2) \ + \ V_2(\mathbf{r}_2) \ + \ V_{12}(\mathbf{r}_2, \mathbf{r}_2)$$

$$T_1(\mathbf{r}_1) \longrightarrow -\frac{\hbar^2}{2m_e}\nabla_{r_1}^{\ 2} \qquad\qquad T_2(\mathbf{r}_1) \longrightarrow -\frac{\hbar^2}{2m_e}\nabla_{r_2}^{\ 2}$$

$$V_1(\mathbf{r}_1) = -\frac{Z\ e^2}{|\mathbf{r}_1|} \quad \longrightarrow \quad -\frac{Z\ e^2}{r_1} \qquad\qquad V_2(\mathbf{r}_2) = -\frac{Z\ e^2}{r_2}$$

$$V_{12}(\mathbf{r}_2, \mathbf{r}_2) \ = \ +\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad \longrightarrow \quad +\frac{e^2}{r_{12}}$$

$$\Psi\left(\mathbf{r}_1, \mathbf{r}_2\right)$$

$$H = T_1(\mathbf{r}_1) \; + \; V_1(\mathbf{r}_1) \; + \; T_2(\mathbf{r}_2) \; + \; V_2(\mathbf{r}_2) \; + \; V_{12}(\mathbf{r}_2, \mathbf{r}_2)$$

$$[T_1(\mathbf{r}_1) \; + \; V_1(\mathbf{r}_1) \; + \; T_2(\mathbf{r}_2) \; + \; V_2(\mathbf{r}_2) \; + \; V_{12}(\mathbf{r}_2, \mathbf{r}_2)] \, \Psi \left(\mathbf{r}_1, \mathbf{r}_2\right) \; = \; E \, \Psi \left(\mathbf{r}_1, \mathbf{r}_2\right)$$

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{r_1}{}^2 \; - \; \frac{Z \; e^2}{r_1} \; - \; \frac{\hbar^2}{2m_e} \nabla_{r_2}{}^2 \; - \; \frac{Z \; e^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\right] \Psi \left(\mathbf{r}_1, \mathbf{r}_2\right) \; = \; E \, \Psi \left(\mathbf{r}_1, \mathbf{r}_2\right)$$

Evaluation of the repulsion term using the multipole expansion

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{LM} \frac{4\pi}{2L+1} \, \frac{r_<^L}{r_>^{L+1}} \, Y^\star_{LM}(\hat{r}_1) \, Y_{LM}(\hat{r}_2) \tag{1}$$

where

$$r_< = r_1, \quad r_> = r_2 \quad \text{for} \quad |\mathbf{r}_1| \; < \; |\mathbf{r}_2|$$
$$r_< = r_2, \quad r_> = r_1 \quad \text{for} \quad |\mathbf{r}_1| \; > \; |\mathbf{r}_2|$$

Evaluation of the matrix element in general case

$$\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \psi^\star_{n_1 l_1 m_1}(\mathbf{r}_1) \, \psi^\star_{n_2 l_2 m_2}(\mathbf{r}_2) \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{n_1 l_1 m_1}(\mathbf{r}_1) \, \psi_{n_2 l_2 m_2}(\mathbf{r}_2) \tag{2}$$

is performed separately over the radial and angular parts

$$\begin{aligned} \int r_1^2 dr_1 \int d\hat{r}_1 \int r_2^2 dr_2 \int d\hat{r}_2 \qquad & R^\star_{n_1 l_1}(r_1) Y^\star_{l_1 m_1}(\hat{r}_1) \, R^\star_{n_2 l_2}(r_2) Y^\star_{l_2 m_2}(\hat{r}_2) \\ \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \qquad & R_{n_1 l_1}(r_1) Y_{l_1 m_1}(\hat{r}_1) \, R_{n_2 l_2}(r_2) Y_{l_2 m_2}(\hat{r}_2) \end{aligned} \tag{3}$$

where $d\hat{r}_i$ means the integration over $d\Omega_i = \sin\theta_i d\theta_i d\varphi_i$.

The evaluation of general case - angular integrals of three Y_{lm}'s

$$C^L = \int Y^{\star}_{l_i m_i}(\theta, \varphi) Y_{LM}(\theta, \varphi) Y_{l_i m_i}(\theta, \varphi) d\Omega \tag{4}$$

For the case of both s-states, $l_i = 0 \quad m_i = 0$ only $L = 0 \quad M = 0$ are non-zero; The sum reduces to one term. The angular factors give value one, since the $(Y_{L=0M=0})^2 = (4\pi)^{-1}$ cancels the corresponding factor in the multipole expansion and due to the normalization.

Thus the repulsion matrix element with the e^2 encluded

$$\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \psi^{\star}_{100}(\mathbf{r}_1) \psi^{\star}_{100}(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) \tag{5}$$

is evaluated as the radial integral only

$$\int r_1^2 dr_1 \int r_2^2 dr_2 R^{\star}_{10}(r_1) R^{\star}_{10}(r_2) \frac{e^2}{r_>} R_{10}(r_1) R_{10}(r_2) \tag{6}$$

Calculating the Radial Integral

Radial Part $R_{1,0}(r)$:

$$R_{1,0}(r) = 2 \cdot \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \cdot e^{-\frac{Z \cdot r}{a_0}} = R^*_{1,0}(r)$$

Integral:

$$\begin{aligned}
&\int_0^\infty \int_0^\infty r_1^2 \cdot r_2^2 \cdot R_{1,0}(r_1)^2 \cdot R_{1,0}(r_2)^2 \frac{e^2}{r_>} dr_1 dr_2 \\
&= \int_0^\infty \int_0^\infty 2^4 \left(\frac{Z}{a_0}\right)^6 e^{-\frac{2Z}{a_0}(r_1+r_2)} r_1^2 \cdot r_2^2 \frac{e^2}{r_>} dr_1 dr_2 \\
&= 2^4 \left(\frac{Z}{a_0}\right)^6 \cdot e^2 \int_0^\infty \int_0^\infty e^{-\frac{2Z}{a_0}(r_1+r_2)} r_1^2 \cdot r_2^2 \frac{1}{r_>} dr_1 dr_2
\end{aligned}$$

With substitutions $\quad \frac{2Z}{a_0} r_1 \rightarrow r_1$ and $\quad \frac{2Z}{a_0} r_2 \rightarrow r_2$

$$= \frac{1}{2} \frac{Ze^2}{a_0} \underbrace{\int_0^\infty \int_0^\infty r_1^2 r_2^2 e^{-r_1} e^{-r_2} \frac{1}{r_>} dr_1 dr_2}_{intA}$$

Observe that $\frac{e^2}{a_0} = 1a.u. = E_0$
To calculate the rest-integral, we split it into two integrals. For each r_1 are we taking the integral over r_2 and than can we take the integrale over r_1:

$$intA = \int_0^\infty \left(\int_0^{r_1} e^{-r_1 - r_2} r_1 r_2^2 dr_2 \right) dr_1 + \int_0^\infty \left(\int_{r_1}^\infty e^{-r_1 - r_2} r_1^2 r_2 dr_2 \right) dr_1$$
$$= \int_0^\infty r_1 e^{-r_1} \underbrace{\int_0^{r_1} r_2^2 e^{-r_2} dr_2}_{intB} dr_1 + \int_0^\infty r_1^2 e^{-r_1} \underbrace{\int_{r_1}^\infty e^{-r_2} r_2 dr_2}_{intC} dr_1$$

With partial integration one get:

$$intB = 2 - e^{-r_1}(r_1^2 + 2r_1 + 2)$$

$$intC = e^{-r_1}(r_1 + 1)$$

And with this you get by again merging the two split integrals:

$$intA = \int_0^\infty 2r_1 e^{-r_1} - e^{-2r_1}(r_1^2 + 2r_1) dr_1$$

We use

$$\int_0^\infty x^n e^{-x} dx = n!$$

If the exponent contains α, we make substitution

$$x = \frac{1}{\alpha} y \qquad\qquad dx = \frac{1}{\alpha}\ dy$$

so that

$$\int_0^\infty \quad x^n \quad dx\ e^{-\alpha x} \quad = \quad \frac{1}{\alpha^{n+1}} \int_0^\infty \quad y^n \quad dy\ e^{-y}$$

We re-write $intA$ as

$$intA = \int_0^\infty 2r_1 e^{-r_1} dr_1 - \int_0^\infty e^{-2r_1} r_1^2 dr_1 - \int_0^\infty e^{-2r_1} 2r_1 dr_1$$

We see that the first integral has $n = 1$ and no constant in the exponential; thus we get 2. Second term contains $n = 2$ and $\alpha = 2$. It thus gives

$$-\frac{1}{2^3} 2! = \frac{1}{4}$$

The third term has $n = 1$ and $\alpha = 2$. It gives

$$-2\frac{1}{2^2} 1! = \frac{1}{2}$$

The final expression for

$$A = \int_0^\infty \int_0^\infty r_1^2 r_2^2 e^{-r_1} e^{-r_2} \frac{1}{r_>} dr_1 dr_2 \tag{7}$$

is thus

$$A = 2 - \frac{1}{4} - \frac{1}{2} = \frac{5}{4}$$

And with this the whole integral becomes

$$\int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \; \psi_{100}^\star\left(\mathbf{r}_1\right) \psi_{100}^\star\left(\mathbf{r}_2\right) \frac{e^2}{\left|\mathbf{r}_1 - \mathbf{r}_2\right|} \psi_{100}\left(\mathbf{r}_1\right) \psi_{100}\left(\mathbf{r}_2\right) = \frac{5}{8} \frac{Ze^2}{a_0} \tag{8}$$

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How to get the variational method for Helium

written by Alexander Sauter; modified by L. Kocbach ; September 2006

We start with hydrogen-like (one electron) problem

$$H = T_1 + V_1.$$

We remember that the kinetic energy contains only second derivatives of the wavefunction, while

$$V_i = -\frac{Ze^2}{r_i}.$$

We know that the ground state energy is

$$E_{1s}(Z) \ = -\frac{1}{2}\ Z^2 \frac{e^2}{a_0}.$$

We will need the virial theorem, in order to avoid unnecessary evaluations. It states:

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

Since

$$\langle H \rangle \ = \ E_{1s}(Z) \ = \ -\frac{1}{2}\ Z^2 \frac{e^2}{a_0} \ = \ -\frac{1}{2}\ Z^2\ E_0$$

and

$$\langle H \rangle = \langle T \rangle + \langle V \rangle$$

we can see that

$$\langle T \rangle \;=\; \frac{1}{2}\, Z^2 \; E_0$$

and

$$\langle V \rangle \;=\; -Z^2 \; E_0$$

Let us now consider the variable, or unknown effective charge number z, which is contained only in the wavefunctions.

When $z \;=\; Z$, the kinetic energy $\langle T \rangle$ is $\frac{1}{2}\; Z^2\; E_0$. As we mentioned, the kinetic energy contains only second derivatives, no Z. That means that when z becomes different from Z, there can not be any Z in the kinetic energy T, thus

$$\langle T(z) \rangle \;=\; \frac{1}{2}\; z^2 \; E_0$$

On the other hand, the potential energy contains Z, as seen above. Thus

$$\langle V(z) \rangle \;=\; -\; z \; Z \; E_0$$

We look now at the total energy for two electrons including the repulsion

$$H = T_1 + T_2 + V_1 + V_2 + V_{12}.$$

The repulsion term V_{12} is known for the hydrogen like orbitals, or repulsion between two electrons where both are in $1s$ orbital. For atomic number Z we obtained

$$V_{12} = \frac{5}{8}\frac{Ze^2}{a_0} = \frac{5}{8}\,Z\,E_0.$$

Again, there is no Z in the repulsion energy operator, therefore

$$V_{12}(z) = \frac{5}{8}\,z\,E_0$$

for the orbitals with effective z.

Thus

$$E(z) = E_0\left(\frac{1}{2}\,z^2 - zZ\right) + E_0\left(\frac{1}{2}\,z^2 - zZ\right) + E_0\frac{5}{8}z.$$

or

$$E(z) = \left(z^2 - 2zZ + \frac{5}{8}z\right)E_0.$$

The variational method says that for the ground state the energy functional

$$E(z) \;=\; \left(z^2 - 2zZ + \frac{5}{8}z\right) E_0.$$

must be extremal:

$$\frac{d}{dz}E(z) = 0$$

$$\Leftrightarrow 2z - 2Z + \frac{5}{8} = 0$$

$$\Leftrightarrow z = Z - \frac{5}{16}.$$

Atomic Units

Unit of length is the Bohr radius:

$$a_0 = \frac{\hbar^2}{m_e e^2} \left(= 4\pi\epsilon_0 \frac{\hbar^2}{m_e e^2} \right)$$

The first is in atomic units, second in SI-units. This quantity can be remembered by recalling the virial theorem, i.e. that in absolute value, half of the potential energy is equal to the kinetic energy. This gives us

$$\frac{1}{2}\frac{e^2}{a_0} = \frac{\hbar^2}{2m_e {a_0}^2}$$

and if we accept this relation, we have the above value of a_0.

The so called fine structure constant

$$\alpha = \frac{e^2}{\hbar c}$$

expresses in general the *weakness* of electromagnetic interaction.

Some Constants and Quantities

$v_0 = \alpha c = 2.187 10^6$ m s$^-1$ Bohr velocity

$a_0 = 0.529177\ 10^{-10}$ m Bohr radius

$\hbar = 0.6582\ 10^{-15}$ eV s Planck's constant

$k_B = 0.8625\ 10^{-4}$ eV $^\circ$K^{-1} Boltzmann constant

R $= N_A k_B$

$N_A = 6.0222\ 10^{23}$ Avogadro's number

$\mu_B = 0.579\ 10^{-4}$ eV (Tesla)$^{-1}$ Bohr magneton

Plank's formula

$$\rho(\omega_{ba}) \;=\; \frac{\hbar\omega_{ba}^3}{\pi^2 c^3}\;\frac{1}{e^{\hbar\omega/kT}-1}$$

Useful formulae and informations

$P_0\,(cos\theta) = 1$ $P_1\,(cos\theta) = cos\theta$