

Hartree's Total Energy $\tilde{E} = \langle \Psi | \mathcal{H} | \Psi \rangle$. Ground-state of a 2e-atom.

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We define the system's total energy by: $\tilde{E} = \langle \Psi | \mathcal{H} | \Psi \rangle$, then -- by (50) --

$$\begin{aligned} \rightarrow \tilde{E} = \langle \Psi | \mathcal{H} | \Psi \rangle &= \sum_k \langle \phi_{n_k} | -\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} | \phi_{n_k} \rangle + \\ &+ \sum_{k>j} \sum_j \langle \phi_{n_j} \phi_{n_k} | \frac{e^2}{r_{jk}} | \phi_{n_j} \phi_{n_k} \rangle. \end{aligned} \quad (52)$$

Now if the ϕ_{n_k} satisfy Hartree's Eqn, Eq. (48), i.e.

$$\rightarrow \left(-\frac{\hbar^2}{2m} \nabla_k^2 - \frac{Ze^2}{r_k} \right) \phi_{n_k} = \left(\epsilon_{n_k} - \sum_{j \neq k} \langle \phi_{n_j} | \frac{e^2}{r_{jk}} | \phi_{n_j} \rangle \right) \phi_{n_k}, \quad (53)$$

then Eq. (52) for \tilde{E} becomes...

$$\rightarrow \tilde{E} = \sum_k \epsilon_{n_k} - \sum_k \sum_{j \neq k} \langle \phi_{n_j} \phi_{n_k} | \frac{e^2}{r_{jk}} | \phi_{n_j} \phi_{n_k} \rangle + \sum_{k>j} \sum_j \langle \phi_{n_k} \phi_{n_j} | \frac{e^2}{r_{jk}} | \phi_{n_k} \phi_{n_j} \rangle. \quad (54)$$

The 2nd term RHS in (54) is twice as large as the 3rd, so we get...

$$\underline{\tilde{E} = \sum_k \epsilon_{n_k} - \sum_{k>j} \sum_j \langle \phi_{n_j} \phi_{n_k} | (e^2/r_{jk}) | \phi_{n_j} \phi_{n_k} \rangle.} \quad (55)$$

We see that the total system energy \tilde{E} is not just the simple sum of the one-electron energies, viz. $E = \sum_k \epsilon_{n_k}$. Although each ϵ_{n_k} is roughly the ionization energy of the k^{th} electron (from state $\phi_{n_k} \rightarrow$ continuum), there is an overall correction (the 2nd term RHS in (55)) -- due to the fact that removal of the k^{th} electron forces an adjustment of the self-consistent fields for the remaining electrons $j \neq k$.

☐ The simple product states $\Psi = \phi(1)\phi(2)\dots\phi(N)$ so far used in Hartree's calculation cannot possibly obey electron exchange symmetry, except in one simple case: the ground state of a 2e-atom. Here, the overall Ψ must be:

$$\rightarrow \Psi(1,2) = \phi(x_1)\phi(x_2), \quad (56)$$

Where $\phi_{n_1} = \phi_{n_2} = \phi$ are both eigenfns of the same form (and a spin singlet wavefn is implicit; the overall state is $|1^1S_0\rangle$). Now Hartree's

First Ionization Energy I for a 2e-Atom.

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problem assumes its simplest (non-trivial) form, viz...

$$\left\{ \begin{aligned} \left[-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{r_1} + G(r_1) \right] \phi(r_1) &= \varepsilon_1 \phi(r_1), \\ \text{w// } G(r_1) &= \int_{\infty} d^3x_2 |\phi(r_2)|^2 \frac{e^2}{r_{12}}. \end{aligned} \right\} \underline{\underline{\text{2e-atom ground state.}}} \quad (57)$$

According to Eq. (55), the total electronic energy of the atom is :

$$\rightarrow \tilde{E} = 2\varepsilon_1 - \bar{G}, \quad \text{w// } \bar{G} = \int_{\infty} d^3x_1 \int_{\infty} d^3x_2 |\phi(r_1)|^2 |\phi(r_2)|^2 \frac{e^2}{r_{12}}. \quad (58)$$

Now, if this 2e-atom becomes singly ionized (i.e. one e is pulled off), left behind will be an ion whose remaining electron has energy : $E_0 = (-) Z^2 (e^2/2a_0)$, where Ze is the nuclear charge*. The energy necessary to do this is ...

$$\underline{\underline{I = E_0 - \tilde{E} = (-)\varepsilon_1 + [\bar{G} - \varepsilon_1 - Z^2(e^2/2a_0)]}}. \quad (59)$$

It is called the first ionization energy for the 2e-atom... it is what is usually calculated -- and then compared with exptl data -- to see how well the theoretical approxns are doing.

ASIDE Difference between I (1st ion^zn energy) and ε_1 (bound state energy).

In accordance with the remark below Eq. (55) -- that ε_1 by itself should be \approx the ionization energy -- we now show that $I \approx -\varepsilon_1$ is a \sim good approxn. Do this by looking at the pair of eqns...

$$\left\{ \begin{aligned} \textcircled{1} \text{ for (ionized) 1e-atom in the ground state: } & \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \right] \phi_0(r) = E_0 \phi_0(r), \\ \textcircled{2} \text{ for (either) e in the 2e-atom ground state: } & \left[-\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} + G(r) \right] \phi(r) = \\ & [G(r) \text{ is defined in Eq. (57)}]. \text{ Multiply } \textcircled{2} \text{ by } \phi_0, \textcircled{1} \text{ by } (-)\phi, \quad \underline{\underline{= \varepsilon_1 \phi(r).}} \end{aligned} \right. \quad (60)$$

add the two resulting eqns, and then carry out the following steps: (1) use Green's Thm to convert the $(\phi_0 \nabla^2 \phi - \phi \nabla^2 \phi_0)$ term to a surface integral that vanishes

* We are talking about the single ionization of He (neutral), or Li^+ , or Be^{++} , etc.

Approxn $I \approx -E_1$ (for 2e-atom). Numerical Results for He.

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as $r \rightarrow \infty$, (2) put in $\bar{G} = \int_{\infty} G(r) [\phi(r)]^2 d^3x$, (3) define $\delta\phi = \phi - \phi_0$, and (4) neglect terms quadratic in the (presumably) small quantity $\delta\phi$. Then, by defining I as in Eq. (59), viz. $I = -E_1 + [\bar{G} - E_1 + E_0]$, we find...

$$\underline{I \approx -E_1 + \int_{\infty} [G(r) - \bar{G}] \phi \delta\phi d^3x.} \quad (61)$$

So I differs from $-E_1$ by a term of relative smallness $\delta\phi/\phi$. This term is made even smaller by the fact that e-e repulsion energy $G(r)$ is a relatively slowly varying fn of r , so the integrand factor $[G(r) - \bar{G}]$ is \sim small. Then $I \approx -E_1$ is not too bad an approxn; the difference is usually $\sim 5\%$.

These arguments can be generalized to N -electron atoms, where Hartree's single-electron energy $|E_{nk}|$ is used as a rough approxn to the ionization energy for that electron. The add-on term in (61) or (60) is a correction \sim few %.

END of ASIDE

Hartree's Eqs (57) for the He atom ($Z=2$) were first solved numerically by W. S. Wilson & R. B. Lindsay, Phys. Rev. 47, 681 (1935) [using mechanical calculators! *]. Their results are graphed below. To specify the calculated one-electron wavefn $\phi(r)$, they defined...

$$\rightarrow \underline{P(r) = r\phi(r)}, \quad \text{norm: } \int_0^{\infty} [P(r)]^2 dr = 1 \quad (62)$$

To measure the fn $G(r)$ [Eq. (57)]--this is the repulsive interaction between one electron considered as a point charge with the other electron considered (per Hartree) as a distribution, Wilson & Lindsay defined...

$$\rightarrow \underline{Z_p(r) = 2 - rG(r);} \quad (63)$$

$Z_p(r)$ may be interpreted as a screening fn. Finally, Wilson & Lindsay found the

* Contrary to legend, these machines were not wood-burning; they used steam power.

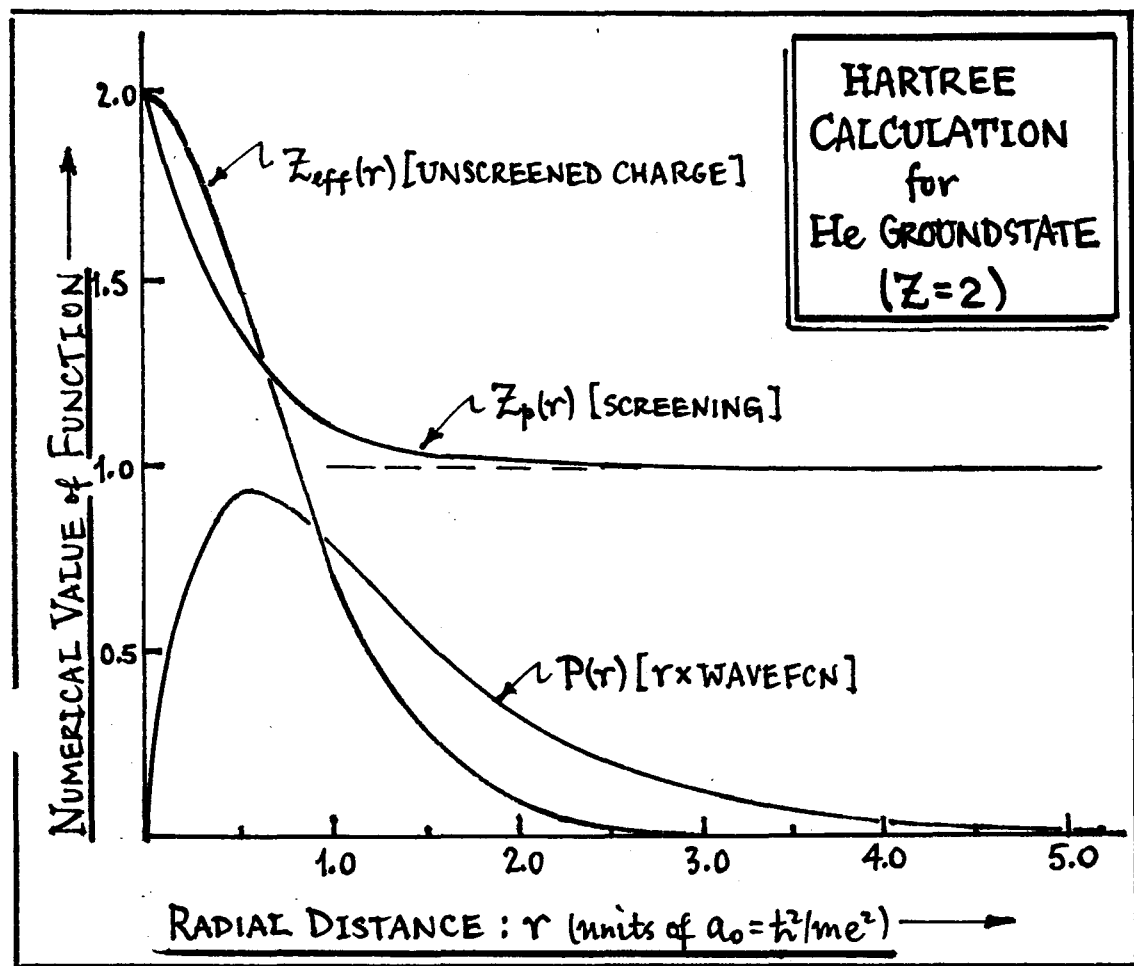
Hartree (per Wilson-Lindsay) first I.P. for He ($Z=2$).

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total charge (including the nucleus) inside radius r , by calculating...

$$\rightarrow \underline{Z_{\text{eff}}(r) = 2 - 2 \int_0^r [P(\xi)]^2 d\xi = 2 \int_r^\infty [P(\xi)]^2 d\xi.} \quad (64)$$



These graphs give a theoretical picture of the charge distribution for one electron in the groundstate of the He atom. Of course, the distributions cannot be observed as such. For comparison with experiment, one must look at some integrated effect. The

(measurable) quantity most often checked is the I.P. I of Eq. (59). For that, the Wilson-Lindsay calculation yielded:

$$\underline{-2E_1 = 49.96 \text{ eV}, \quad G(0) = 45.91 \text{ eV},} \leftarrow \text{Wilson-Lindsay results,} \quad (65)$$

and the wavefn value: $(P/r)|_{r=0} = \phi(0) = 4.755$. From the above graph of $P(r)$ & $G(r)$ vs. r , one can evaluate: $\bar{G} = \int_0^\infty G(r) [P(r)/r]^2 d^3x = 27.95 \text{ eV}$. So...

$$\underline{I = -2E_1 + \bar{G} - 4 \times 13.606 \text{ eV} = +23.49 \text{ eV},} \leftarrow \text{Wilson-Lindsay first I.P.} \quad (66)$$

NOTE: as advertised in above ASIDE [Eqs. (60)-(61)], in fact $I \approx -E_1 = 24.98 \text{ eV}$; I is just about 6% below $|E_1|$. The exptl value is: $\underline{I_{\text{EXP}} = 24.59 \text{ eV}}$, so the theory is $\approx 4.5\%$ too small. Other techniques (esp. variational) can produce I -

Exchange Symmetry Corrections via $\Psi = \text{Slater Determinant}$.

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values that are of comparable accuracy ($\sim 5\%$), with much less computational complexity. However, those techniques give little, if any, accurate information about the one-electron wavefn $\phi(r) = \frac{1}{r} P(r)$ in He. The "elementary" Hartree calculation we have outlined does produce a "reasonable" version of $\phi(r)$.

□ Finally, we comment on corrections to the primitive Hartree formulation which follow from properly considering electron exchange symmetry. The effects of exchange were worked out by Fock[†] (and later, Slater), and the resulting formalism is known as Hartree-Fock theory. The major new input is to replace Hartree's product wavefn $\Psi = \phi_\alpha(1)\phi_\beta(2)\dots\phi_\mu(N)$ by the "Slater Determinant Wavefn" [discussed on p. ip 14; see Eqs. (35)-(36)], viz.

from one-electron eigenfn $\left\{ \begin{array}{l} \varphi_\lambda(k) = \phi_\lambda(r_k) \chi(\sigma_k) \end{array} \right. \begin{array}{l} \phi_\lambda(r_k) = \text{space state } (\phi_\lambda \sim \text{soln. of Eq. (48)}), \\ \chi(\sigma_k) = |S_k, m_k\rangle = \text{spin state } (S_k = \frac{1}{2}, m_k = \pm \frac{1}{2}); \end{array}$

construct
$$\underline{\underline{\Psi(1,2,\dots,N)}} = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \varphi_\alpha(1) & \varphi_\alpha(2) & \dots & \varphi_\alpha(N) \\ \varphi_\beta(1) & \varphi_\beta(2) & \dots & \varphi_\beta(N) \\ \vdots & \vdots & & \vdots \\ \varphi_\mu(1) & \varphi_\mu(2) & \dots & \varphi_\mu(N) \end{bmatrix} \quad (67)$$
 Each of the $N!$ terms in Ψ is an N -fold product of the $\varphi_\lambda(k)$, with all possible permutations of

$\lambda \neq k$ [for N electrons, $k=1,2,\dots,N$, and the eigenindex $\lambda=\alpha,\beta,\dots,\mu$ takes on N different values]. This Ψ obeys the Pauli Exclusion Principle (no two e 's in same state), and has the proper exchange symmetry for fermions ($\Psi \rightarrow -\Psi$ upon exchange of any two electrons). The $\varphi_\lambda(k)$ are normed so that: $\int \varphi_\alpha^*(k) \varphi_\beta(k) d\tau_k = \delta_{\alpha\beta}$, with the integration over $d\tau_k$ including both the space & spin cds of the k^{th} electron. Then $\int d\tau_1 \dots \int d\tau_N |\Psi|^2 = 1$, etc.

To derive an exchange-corrected version of Hartree's Eqn [Eq. (48)], Fock

[†] V.A. Fock, Zeits. für Physik 61, 126 (1930); 62, 795 (1930).

Hartree-Fock Eqns. Fock's Exchange Correction.

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imposed: $\delta \langle \Psi | \mathcal{H} | \Psi \rangle = 0$, \mathcal{H} the N-electron Hamiltonian in Eq. (44) and Ψ the Slater Determinant in Eq. (67). This generates the so-called Hartree-Fock Eqns, and it capitalizes on the connection with the variational (minimum energy) principle discussed in Eqs. (49)-(51) above. The actual derivation of the Hartree-Fock Eqns is algebraically complicated--details can be found in, e.g., H.A. Bethe "Intermediate QM" (W.A. Benjamin Co., 1964), Chap. 6. The result is...

$$(H_k - \epsilon_{n_k}) \phi_{n_k}(\mathbf{r}_k) = \sum_{j \neq k} \delta_{m_j m_k} \left[\int_{\infty} \phi_{n_j}^*(\mathbf{r}_j) \frac{e^2}{r_{jk}} \phi_{n_k}(\mathbf{r}_j) d^3 x_j \right] \phi_j(\mathbf{r}_k) \quad (68)$$

Here H_k is Hartree's one-electron Hamiltonian (i.e. the [] LHS in (48)); Hartree's (primitive) Eqn is just: $(H_k - \epsilon_{n_k}) \phi_{n_k}(\mathbf{r}_k) = 0$. The new term RHS in (68) is a correction exclusively due to imposing exchange symmetry, i.e. using $\Psi(\text{FOCK}) = \text{Slater Determinant}$, rather than $\Psi(\text{HARTREE}) = \text{product states}$.

REMARKS On Fock's Exchange Correction Term.

1. Because of the Kronecker delta $\delta_{m_j m_k}$ in Fock's term, the exchange correction for electron #k contributes only from electrons $j \neq k$ which have the same spin direction. Such electrons are "spin-correlated".
2. Fock's term depends on exchange integrals $\langle n_j | e^2/r_{jk} | n_k \rangle$ over the e-e repulsion potential [the j^{th} & k^{th} electrons effectively exchange their quantum states $n_k \leftrightarrow n_j$ in such integrals]. This is not surprising, in view of our previous discussion of exchange effects [Eqs. (21)-(25), Eqs. (27)-(31), above].
3. The Hartree-Fock Eqns (68) are not yet the last word for the N-electron problem. The main Hamⁿ \mathcal{H} [Eq. (44)] from whence they came, still does not incorporate magnetic dipole-dipole interactions; e.g. it ignores spin-orbit (i.e. $\mathbf{L} \cdot \mathbf{S}$) coupling. This can be added... but we shall bail out here and now.