**28** [15 pts]. In the Thomas-Fermi atom, the total e-e repulsion energy can be written:
$E_{ee} = \frac{1}{2} \int U_e(r) n(r) dV$, $^{w/}$ $U_e(r) =$ potential energy of one $e$ in the presence of the the other $e$'s, and $n(r) =$ number density of electron states [$n$ replaces the $\rho$ in Eq. (39), p. ip 17, class notes]. In turn: $U_e(r) = U(r) + \frac{Ze^2}{r}$, $^{w/}$ $U(r)$ the full T-F potential [$U(r)$ is (-)ve]; the nuclear attraction $(-Ze^2/r)$ has been subtracted out.

(A) Show that: $\underline{E_{ee} = -\frac{1}{2} E_{en} - \frac{5}{6} K_e}$, $^{w/}$ $E_{en}$ is the total electron-nuclear binding energy, and $K_e$ is the total electronic kinetic energy.

(B) Use the Virial Theorem for the Coulomb field to show: $\boxed{E_{ee} = -\frac{1}{7} E_{en}}$. Thus, in the T-F atom, the e-e repulsion is relatively small compared to the binding.

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**29** [25 pts]. In the ground state of a two-electron atom, both $e$'s are in 1s orbitals ($^{w/}$ one spin up and the other down $\Rightarrow$ spin singlet). If we neglect magnetic interactions, the system Hamiltonian is: $\mathcal{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - Ze^2(\frac{1}{r_1} + \frac{1}{r_2}) + e^2/r_{12}$, $^{w/}$ $Z$ the nuclear charge and $r_{12}$ the relative cd. If we neglect the e-e repulsion term, the problem reduces to each $e$ moving $\underline{separately}$ in a Coulomb field $-Ze^2/r$; then for each $e$ the energy is $-\frac{1}{2} Z^2 e^2/a_0$ ($a_0 = \hbar^2/me^2 =$ Bohr radius), and $\phi(r) = \frac{1}{\sqrt{\pi}}(Z/a_0)^{\frac{3}{2}} e^{-Zr/a_0}$ is its wavefunction. The overall system energy & wavefcn would be: $E_0 = -Z^2 e^2/a_0$ & $\Psi_0(1,2) = \phi(r_1)\phi(r_2)$. Here we want to improve on this zeroth order approximation by a variational calculation which accounts for the e-e repulsion term.

(A) Use a trial wavefcn of form: $\underline{\Psi(1,2) = \mathcal{N} \exp[-\frac{\zeta}{a_0}(r_1 + r_2)]}$, $^{w/}$ $\zeta$ a variational parameter. Adjust the norm cnst $\mathcal{N}$ so that: $\int d^3x_1 \int d^3x_2 |\Psi(1,2)|^2 = 1$.

(B) Calculate the energy: $E(\zeta) = \langle \Psi | \mathcal{H} | \Psi \rangle$. The K.E. & P.E. integrals here are easy. Deal with the e-e repulsion term by expanding $1/r_{12}$ via the Spherical Harmonic Addition Theorem [e.g. Jackson, Sec. 3.6]. Show: $\int d^3x_1 \int d^3x_2 |\Psi|^2/r_{12} = \frac{5}{8} \zeta/a_0$.

(C) Minimize $E(\zeta)$ w.r.t. $\zeta$ and find $E_{min}$. Approximate the first ionization potential of the atom by: $\underline{I(Z) = -E_{min} - \frac{1}{2}Z^2 e^2/a_0}$. Calculate $I(Z)$ in Rydbergs (i.e. energy units of $e^2/2a_0 = 13.6$ eV), and compare with the experimental values given in the box.

| $I(Z)$ (Ryd.) | $H^-$ | $He$ | $Li^+$ | $Be^{2+}$ | $B^{3+}$ |
|---|---|---|---|---|---|
| | 0.055 | 1.807 | 5.559 | 11.311 | 19.063 |

(D) Do your $I(Z)$'s agree $^{w/}$ R.T. Robiscoe, Am. J. Phys. $\underline{43}$, 538 (1975)? Why not?

# A variational Hartree-type calculation

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*The ground state of the two-electron atom is treated by a calculation, suggested by Slater, which combines features of both the variational method and Hartree's method of self-consistent fields (SCF). The calculation is mathematically simple, and it exposes the basic physics of the SCF method in a clear and direct way. The result for the first ionization potential for the two-electron atom is in good agreement with experimental values for atomic number $Z \geq 2$.*

## I. INTRODUCTION

Most courses in modern physics at the senior undergraduate level, or in quantum mechanics at the first-year graduate level, make some mention of Hartree's self-consistent field (SCF) method for treating multielectron atoms.[1] Because the SCF method is based on the solution of simultaneous, coupled, nonlinear, integro-differential equations, it is often decided by both instructor and student that a detailed solution is not feasible without use of a computer, and the student is not often asked to do a problem employing the SCF method. As a possible consequence, the student may not fully appreciate the physical content of Hartree's theory. To remedy that situation, should it arise, we present here an explicit, analytic solution of a Hartree-type variational problem which was suggested by Slater[2] and which has the virtues of direct physical appeal, calculational simplicity, and a result in good agreement with experiment. We believe that the method of solution illustrates the physical content of SCF theory in a particularly lucid manner and, thus, may be of some pedagogical value.

## II. TWO-ELECTRON ATOM

The problem we shall do is perhaps the simplest of all Hartree-type problems, namely the calculation of the first ionization potential $I$ for the ground state of a two-electron atom of nuclear charge $Ze$. With each electron described by a space wave function $u(r_k)$, $k = 1, 2$, the Hartree problem here for the "first" electron is

$$[-(\hbar^2/2m)\nabla_1^2 - (Ze^2/r_1) + G(r_1)]u(r_1) = E_1 u(r_1), \quad (1)$$

where $G(r_1)$ is the interaction of the first electron with the central field produced by the second electron, namely

$$G(r_1) = \int |u(r_2)|^2 (e^2/r_{12}) d\tau_2 \quad (2)$$

with $r_{12}$ the interelectron separation. The total system energy is $E = 2E_1 - \bar{G}$, where $\bar{G}$ is the average electron–electron repulsion energy:

$$\bar{G} = \int |u(r_1)|^2 G(r_1) d\tau_1. \quad (3)$$

The desired first ionization potential $I$ is the difference between $E$ and the energy $-Z^2(e^2/2a_0)$ of the one-electron atom; that is,

$$I(Z) = \bar{G} - 2E_1 - Z^2(e^2/2a_0), \quad (4)$$

where $a_0 = \hbar^2/me^2$ is the first Bohr radius.

Now an explicit calculation according to the Hartree formulation of this problem could be done by using simple trial wave functions of the screened hydrogenic type, namely

$$u(r_k, \alpha_k) = (\alpha_k^3/\pi)^{1/2} \exp(-\alpha_k r_k) \quad (5)$$

(which is properly normalized), where the $\alpha_k$ are variational parameters which are adjusted to minimize the total system energy $E$. However, even this calculation proves to be tedious, and one runs into the usual difficulties in evaluating the electron–electron repulsion energy $G$, which is "conveniently" done in elliptic coordinates. The mathematical details of this exercise are sufficiently involved so that physical insight may easily be lost.

Slater's formulation of this problem avoids much of the mathematical detail by concentrating on only one electron and using the approximation that $I \approx -E_1$. This often used approximation is reasonable insofar as $E_1$ is the assigned single-electron eigenenergy in the Hartree problem, and it can be justified by direct calculation (see remarks in Sec. IV).[3] Variational wave functions of the type defined in Eq. (5) are used, and expectation values of the one-electron potential and kinetic energies are calculated straightforwardly. The sum of these energies is the total energy $E_1(\alpha_1, \alpha_2)$ of the first electron in the presence of the second. This result for $E_1$ is then minimized with respect to $\alpha_1$, and $\alpha_2$ is set equal to $\alpha_1$ for self-consistency. Imposing $\alpha_2 = \alpha_1$ not only treats the ground state electrons as being equivalent but also satisfies the required even exchange symmetry of the space part of the ground state wave function. The result for the ionization energy $I$ calculated in this way agrees quite well with experiment. In the next section, we carry out the details of this method of solution.

## III. SLATER'S PROBLEM

We begin by calculating the potential of one electron, considered as a point charge, in the field of the other electron, considered as having a charge density $\rho(r, \alpha)$

$= - e |u(r, \alpha)|^2$, where $u(r, \alpha)$ is given by Eq. (5). The electric field due to $\rho(r, \alpha)$ at distance $r$ from the nucleus is then of magnitude

$$E(r, \alpha) = (4\pi/r^2) \int_0^r \rho(x, \alpha) x^2 \, dx$$

$$= - (4e/\alpha^3) \int_0^r x^2 \exp(- 2\alpha x) \, dx. \qquad (6)$$

After a straightforward integration, we find

$$E(r, \alpha) = - (e/r^2)\{1 - [1 + 2(\alpha r)$$

$$+ 2(\alpha r)^2] \exp(- 2\alpha r)\}. \qquad (7)$$

The work necessary to bring a charge $- e$ from $\infty$ up to $r$ against this field is given by

$$W(r, \alpha) = e \int_\infty^r E(x, \alpha) \, dx. \qquad (8)$$

Another straightforward integration produces the result

$$W(r, \alpha) = (e^2/r)[1 - (1 + \alpha r) \exp(- 2\alpha r)]. \qquad (9)$$

Adding the nuclear potential $- Ze^2/r$ to $W(r, \alpha)$, we get the total potential energy $U(r, \alpha)$ of one (point) electron in the presence of the nucleus and of the second (distributed) electron:

$$U(r, \alpha) = - (e^2/r)[(Z - 1) + (1 + \alpha r) \exp(- 2\alpha r)]. \quad (10)$$

This $U(r, \alpha)$ exhibits the expected behavior: $U(r, \alpha) \approx (Z - 1)e^2/r$ for $r \to \infty$, which is the nuclear potential fully shielded by the electron left behind, and $U(r, \alpha) \approx - Ze^2/r$ for $r \to 0$, which is the unshielded nuclear potential.

Now, in the spirit of Hartree's formulation of the problem, we assume that the first electron has a wave function $u(r, \alpha_1)$ and "sees" the potential $U(r, \alpha_2)$ generated by the nucleus and the second electron. The average potential energy of the first electron is then the expectation value

$$U_1(\alpha_1, \alpha_2) = \langle u(r, \alpha_1) | U(r, \alpha_2) | u(r, \alpha_1) \rangle$$

$$= - 4e^2 \alpha_1^3 \int_0^\infty \exp(- 2\alpha_1 r)$$

$$\times [(Z - 1) + (1 + \alpha_2 r) \exp(- 2\alpha_2 r)] r \, dr. \quad (11)$$

Integrating, we easily obtain

$$U_1(\alpha_1, \alpha_2) = - e^2[Z\alpha_1 - \alpha_1 \alpha_2(\alpha_1^2$$

$$+ 3\alpha_1 \alpha_2 + \alpha_2^2)(\alpha_1 + \alpha_2)^{-3}]. \qquad (12)$$

The second term on the right-hand side of this expression is evidently the average electron–electron repulsion

energy $\bar{G}$ [as defined in Eqs. (2) and (3)] for our particular choice of wave functions. In fact, this can be shown to be the case by suitably integrating Eq. (3) over $r_{12}$, but the integration is considerably more difficult.[4]

Next, we calculate the average value of the kinetic energy of the first electron. This is the expectation value

$$T_1(\alpha_1) = \langle u(r, \alpha_1) | T_{op} | u(r, \alpha_1) \rangle, \qquad (13)$$

where $T_{op} = - (\hbar^2/2m)\nabla^2$. Using just the radial part of the Laplacian operator, we get

$$T_1(\alpha_1) = \frac{2\hbar^2 \alpha_1^4}{m}$$

$$\times \int_0^\infty \exp(- \alpha_1 r) \frac{d}{dr} [r^2 \exp(- \alpha_1 r)] \, dr$$

$$= (\hbar \alpha_1)^2/2m, \qquad (14)$$

where it is easiest to integrate by parts.

The total energy of the first electron is now $E_1 = T_1 + U_1$. At this point, there is a clear advantage in adopting atomic units for the problem, which means to measure the variational parameters $\alpha_k$ in units of the inverse Bohr radius $1/a_0 = me^2/\hbar^2$, and to measure the energy in Hartrees (i.e., in units of $e^2/a_0$). Then the expression for the total energy $E_1$ becomes dimensionless and can be written as

$$\epsilon_1(\alpha_1, \alpha_2) = \tfrac{1}{2}\alpha_1^2 - [Z\alpha_1 - \alpha_1\alpha_2(\alpha_1^2$$

$$+ 3\alpha_1\alpha_2 + \alpha_2^2)(\alpha_1 + \alpha_2)^{-3}]. \qquad (15)$$

Treating the electrons as being independent, we next minimize $\epsilon_1$ with respect to $\alpha_1$; that is, we impose $\partial \epsilon_1/\partial \alpha_1 = 0$. This condition straightforwardly leads to

$$\alpha_1 = Z - \alpha_2^3(4\alpha_1 + \alpha_2)(\alpha_1 + \alpha_2)^{-4}. \qquad (16)$$

Now we impose self-consistency by requiring $\alpha_2 = \alpha_1$; this ensures that the Hartree-type central fields $U(r, \alpha_k)$ of Eq. (10) are equivalent for both electrons.[5] With $\alpha_2 = \alpha_1 = \alpha$, Eq. (16) yields

$$\alpha = Z - \sigma, \quad \sigma = 5/16. \qquad (17)$$

The screening constant $\sigma$ derived here is the same as that obtained by the Ritz variational method for this problem.[6] This is not accidental: For our choice of wave functions, the Hartree and Ritz methods are mathematically similar, although conceptually different.

With this result, the total energy of either electron is

$$\epsilon_1(\alpha, \alpha) = \tfrac{1}{2}\alpha^2 - (Z - \tfrac{5}{8})\alpha, \qquad (18)$$

in Hartrees. Taking the first ionization potential $I$ to be

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Table I. Ionization potentials (rydbergs).

|                  | H⁻    | He⁰   | Li⁺   | Be²⁺   | B³⁺    |
|------------------|-------|-------|-------|--------|--------|
| $I(Z)$, experiment | 0.055 | 1.807 | 5.559 | 11.311 | 19.063 |
| $I(Z)$, theory     | 0.043 | 1.793 | 5.543 | 11.293 | 19.043 |
| Difference       | 0.012 | 0.014 | 0.016 | 0.018  | 0.020  |
| % difference     | 21.8  | 0.77  | 0.29  | 0.16   | 0.10   |

(approximately) the negative of this, we obtain (in rydbergs)[7]

$$I(Z) = (Z - 5/16) \times (Z - 15/16). \qquad (19)$$

## IV. CONCLUSION

A comparison between the present theoretical value for the ionization potential $I(Z)$ of Eq. (19) and the experimental value[8] is presented in Table I for the cases $Z = 1-5$, that is, for the two-electron atoms H⁻ through B³⁺. With the exception of H⁻, agreement between experiment and theory is quite good; the percent difference is $< 1\%$ for He⁰ and of the order of 0.1% for B³⁺. That the percent difference decreases with increasing $Z$ can be expected because the electron–nucleus attraction becomes relatively more dominant than the electron–electron repulsion for increasing $Z$, which thus renders the atom more hydrogenic.

The good agreement between $I(Z)$ and experiment for $Z \geq 2$ and the fact that the present calculation predicts a $(1s)^2$ bound state for H⁻ (with binding energy $\approx 0.58$ eV) are somewhat misleading. The reason is that we have made the approximation $I \approx -E_1$, when in fact $I$ should be defined as in Eq. (4). If we adopt the latter definition, then it can be shown[3] that our present $I(Z)$ of Eq. (19) should be reduced by an amount

$$\Delta I \approx \int u(r)[u_0(r) - u(r)][G(r) - \bar{G}] d\tau, \qquad (20)$$

where $u(r)$ is the solution of Hartree's Eq. (1), $u_0(r)$ is the ground state eigenfunction of the one-electron atom, and $G(r)$ and $\bar{G}$ are defined in Eqs. (2) and (3). In the present case, this correction is of order $\sigma^2 = 0.098$ Ry, and is

enough to unbind the H⁻ state as well as to make the agreement between our $I(Z)$ and experiment for $Z \geq 2$ not quite so good.

In summary, we have presented a physical approach to the Hartree formulation of the ground state problem for a two-electron atom. Assumed electron charge distributions are used to calculate actual average fields and potentials within the atom, and the interaction energies are then calculated directly as expectation values. The choice of simple hydrogenic wave functions with a variational screening parameter for the electron distributions leads to an approximate value for the first ionization potential of the atom that is in good agreement with experiment for nuclear charge $Z \geq 2$. At all points, the calculation is mathematically simple and the physics is direct. The method can be extended successfully to the calculation of the excited state energies of the two-electron atom, although if it is desired to distinguish between singlet and triplet states the requirements of exchange symmetry complicate the allowed choice of trial wave function.

[1]See R. M. Eisberg, *Fundamentals of Modern Physics* (Wiley, New York, 1967), Chap. 13, Sec. 3, or L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1968), 3rd ed., Chap. 12, p. 431.

[2]J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill, New York, 1968), 2nd ed., Chap. 7, problems 1–4 on p. 154.

[3]H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Academic, New York, 1957), Sec. 31, pp. 144–145.

[4]The integration method for integrals over $r_{12}$ is indicated in H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand, Princeton, NJ, 1956), 2nd ed., Sec. (11.19), pp. 382–383.

[5]It would be incorrect to require the self-consistency condition $\alpha_2 = \alpha_1$ before the variational condition $\partial \epsilon_i / \partial \alpha_1 = 0$ of Eq. (16), for then we would not be treating $\alpha_1$ and $\alpha_2$ as independent variational parameters.

[6]See Schiff, Ref. 1, p. 257; Bethe and Salpeter, Ref. 3, p. 146; or Margenau and Murphy, Ref. 4, p. 380.

[7]One rydberg $(e^2/2a_0) = 0.5$ hartree $(e^2/a_0)$. We hope that Rydberg would not have been dismayed by this fact.

[8]The experimental values of $I(Z)$ are taken from C. E. Moore, *Atomic Energy Levels*, Nat. Bur. Std. Circ. No. 467 (U.S. GPO, Washington, DC, 1949).

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㉘ [15 pts.]. Size of the e-e repulsion term in the Thomas-Fermi atom.

(A)

1) With $U_e = U + Ze^2/r$, and $n$ the electron # density, the e-e repulsion is :

$$\rightarrow E_{ee} = \tfrac{1}{2}\int (Ze^2/r)\, n\, dV + \tfrac{1}{2}\int U n\, dV. \qquad (1)$$

But, by the basic TF relation $\begin{bmatrix} \text{class} \\ \text{notes} \end{bmatrix}$, p. ip 17, Eq (39) $\Big]$ : $\underline{n = [-2mU]^{\frac{3}{2}}/3\pi^2\hbar^3}$,

so : $\underline{U = -(3\pi^2)^{\frac{2}{3}}\dfrac{\hbar^2}{2m} n^{\frac{2}{3}}}$. This can be used in the 2nd term RHS in (1). For the 1st term RHS, we immediately recognize it as $-\tfrac{1}{2} E_{en}$, $^w/$ $E_{en}$ the total electron-nuclear interaction energy. Then...

$$\rightarrow E_{ee} = -\tfrac{1}{2} E_{en} - (3\pi^2)^{\frac{2}{3}}\dfrac{\hbar^2}{4m}\int n^{\frac{5}{3}}\, dV. \qquad (2)$$

2) The 2nd-term RHS in (2) is related to the total electron kinetic energy $K_e$, as follows. The # states/unit volume in k-space is : $dn = \dfrac{1}{\pi^2} k^2 dk$ [footnote on p. ip 16], or : $\underline{dn = (1/\pi^2\hbar^3)\, p^2 dp}$, in terms of electron momentum $p$. To find the $n$ that appears in Eq. (2), we integrate this up to a max momentum $p_M$ :

$$\left[\!\!\left[ dn = (1/\pi^2\hbar^3)\, p^2\, dp \rightarrow n = \int_0^{p_M} dn = (1/3\pi^2\hbar^3)\, p_M^3, \quad ^{So}/ \quad \underline{p_M = (3\pi^2\hbar^3 n)^{\frac{1}{3}}}, \quad (3) \right.\right.$$

The electron K.E. per unit (spatial) volume is :

(substitute)

$$\dfrac{dK_e}{dV} = \int_0^{p_M}(p^2/2m)\, dn = \dfrac{1}{2m\pi^2\hbar^3}\int_0^{p_M} p^4\, dp = \dfrac{p_M^5}{10m\pi^2\hbar^3} = \dfrac{(3\pi^2\hbar^3)^{5/3}}{10m\pi^2\hbar^3} n^{\frac{5}{3}}$$

$^{So}/$ $\underline{K_e = (3\pi^2)^{\frac{2}{3}}\dfrac{3\hbar^2}{10m}\int n^{\frac{5}{3}}\, dV.}$ $\qquad\qquad (4)$

Compare this $K_e$ with the 2nd term in (2). We see we can write, as desired :

$$\boxed{E_{ee} = -\tfrac{1}{2} E_{en} - \tfrac{5}{6} K_e} \qquad\qquad (5)$$

3) For motion in a Coulomb field, the virial theorem [Davydov, ¶ 17, Eq. (17.15)] prescribes : $2\langle K\rangle = -\langle U\rangle$, or : $\underline{K_e = -\tfrac{1}{2}(E_{ee} + E_{en})}$, in the present case. When used in (5), this gives for the e-e repulsion, as advertised...

$$\boxed{E_{ee} = -\tfrac{1}{7} E_{en}} \leftarrow \text{ee repulsion is only 14\% of binding energy.} \qquad (6)$$

φ507 Solutions

㉙ [25 pts.]. Variational analysis of ground state of 2e atom $^{w/}$nuclear charge $Z$.

(A)

**1.** Normalization of the trial wavefcn : $\underline{\psi(1,2) = N \exp\left[-\frac{\zeta}{a_0}(r_1+r_2)\right]}\ldots$

$$1 = \int d^3x_1 \int d^3x_2 |\psi(1,2)|^2 = |N|^2 \int_0^\infty 4\pi r_1^2\, dr_1 \int_0^\infty 4\pi r_2^2\, dr_2\, e^{-\frac{2\zeta}{a_0}(r_1+r_2)}$$

$^{or/}$ $1 = |N|^2 \left[4\pi \int_0^\infty r^2 e^{-\frac{2\zeta}{a_0}r}\, dr\right]^2 = |N|^2 \left[\pi(a_0/\zeta)^3\right]^2 \Rightarrow \boxed{N = \frac{1}{\pi}\left(\frac{\zeta}{a_0}\right)^3}$ (1)

NOTE: each one-electron wavefcn norms to 1 when $\phi(r) = \sqrt{N}\, e^{-\zeta r/a_0}$.

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(B)

**2.** The system energy $E(\zeta) = \langle\psi|\mathcal{H}|\psi\rangle$ splits into 3 terms…

$$\rightarrow E(\zeta) = E_K(\zeta) + E_r(\zeta) + E_{ee}(\zeta) \tag{2}$$

$^{25/}$ $E_K(\zeta) = -\frac{\hbar^2}{2m}\int d^3x_1 \int d^3x_2\, \psi(\nabla_1^2 + \nabla_2^2)\psi$  $\qquad \nabla^2 = \frac{1}{r}\frac{\partial^2}{\partial r^2}(r$

$$= -\frac{\hbar^2}{2m}N^2 \int_0^\infty 4\pi r_1^2\, dr_1 \int_0^\infty 4\pi r_2^2\, dr_2\, e^{-\frac{\zeta}{a_0}(r_1+r_2)}[\nabla_1^2 + \nabla_2^2]e^{-\frac{\zeta}{a_0}(r_1+r_2)}$$

$$= -\frac{\hbar^2}{2m}(4\pi N)^2 \left\{ \int_0^\infty r_2^2 e^{-\frac{2\zeta}{a_0}r_2}\, dr_2 \int_0^\infty r_1^2 \left[e^{-\frac{\zeta}{a_0}r_1}\nabla_1^2 e^{-\frac{\zeta}{a_0}r_1}\right]dr_1 + \right.$$

$$\left. + \int_0^\infty r_1^2 e^{-\frac{2\zeta}{a_0}r_1}\, dr_1 \int_0^\infty r_2^2 \left[e^{-\frac{\zeta}{a_0}r_2}\nabla_2^2 e^{-\frac{\zeta}{a_0}r_2}\right]dr_2 \right\} \;\bigstar$$

$$= \frac{\hbar^2}{2m}\left(4\frac{\zeta^3}{a_0^3}\right)^2 \cdot 2\left\{\frac{a_0^3}{4\zeta^3}\int_0^\infty \left(\frac{\partial}{\partial r}[r e^{-\zeta r/a_0}]\right)^2 dr\right\}\ldots \text{ put } u = \zeta r/a_0$$

$^{i.e./}$ $E_K(\zeta) = \frac{4\hbar^2}{m}(\zeta^2/a_0^2)\int_0^\infty \left(\frac{\partial}{\partial u}[u e^{-u}]\right)^2 du = \zeta^2 e^2/a_0.$ (3)

$^{&/}$ $E_r(\zeta) = -Ze^2 \int d^3x_1 \int d^3x_2\, \psi\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi$

$$= -Ze^2(4\pi N)^2 \cdot 2 \int_0^\infty r_1\, dr_1\, e^{-2\zeta r_1/a_0}\int_0^\infty r_2^2\, dr_2\, e^{-2\zeta r_2/a_0}$$

$^{i.e./}$ $E_r(\zeta) = -Ze^2(\zeta/a_0)\cdot \int_0^\infty v e^{-v}\, dv \int_0^\infty w^2 e^{-w}\, dw = -2Z\zeta e^2/a_0.$ (4)

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**3.** We now have the first two terms RHS in Eq. (2). For the ee repulsion term, use the spherical harmonic expansion of $1/r_{12}$ [e.g. Jackson Sec. 3.6, Eq. (3.70)]. In

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$\bigstar$ For fcns of $r$ such that $\lim_{r\to\infty}[r f(r)] = 0$, the following identity is useful :

$$\int_0^\infty r^2\, dr\, [f(r)\nabla^2 f(r)] = -\int_0^\infty dr\, \left(\frac{\partial}{\partial r}[r f(r)]\right)^2$$

the present case, since $\psi$ has no $\phi$ dependence, only the $l=0$, $m=0$ term survives the $\phi$ lar integration, and the $1/r_{12}$ expansion effectively degenerates to:

$$\frac{1}{r_{12}} = \begin{cases} 1/r_1, & \text{when } r_1 > r_2; \\ 1/r_2, & \text{when } r_1 < r_2. \end{cases} \quad \Big\rangle \text{ no } \phi \text{ dependence for ground state } \psi. \qquad (5)$$

So the e-e repulsion term in (2) amounts to...

$$E_{ee}(\zeta) = \int d^3x_1 \int d^3x_2 \frac{e^2}{r_{12}} |\psi|^2 = (4\pi N)^2 e^2 \int_0^\infty r_1^2 \, dr_1 \int_0^\infty r_2^2 \, dr_2 \frac{1}{r_{12}} e^{-\frac{2\zeta}{a_0}(r_1+r_2)}$$

$$= (4\pi N)^2 e^2 \int_0^\infty r_1^2 \, dr_1 \, e^{-\frac{2\zeta}{a_0}r_1} \left\{ \int_0^{r_1} r_2^2 \, dr_2 \frac{1}{r_1} e^{-\frac{2\zeta}{a_0}r_2} + \int_{r_1}^\infty r_2^2 \, dr_2 \frac{1}{r_2} e^{-\frac{2\zeta}{a_0}r_2} \right\}$$

i.e.,

$$\underline{E_{ee}(\zeta) = \frac{5}{8} \zeta e^2/a_0.} \qquad (6)$$

Combining Eqs. (3), (4) & (6), we have the total ground state energy $E(\zeta)$ of (2).

**4.** The total ground state energy, in terms of the variational parameter $\zeta$, is

$$E(\zeta) = \left( \zeta^2 - 2Z\zeta + \frac{5}{8}\zeta \right) e^2/a_0 ;$$

soln $\partial E/\partial\zeta = 0 \Rightarrow \underline{\zeta = Z - \frac{5}{16}} = \zeta_m$ $\Big\}$ $\underline{E_{min}(Z) = -\left(Z - \frac{5}{16}\right)^2 e^2/a_0.} \qquad (7)$

(of course: $E_{min}(Z) = E(\zeta_m)$). The approximate first ionization energy is:

$$\boxed{I(Z) = -E_{min}(Z) - \frac{1}{2}Z^2 e^2/a_0 = \left[2\left(Z - \frac{5}{16}\right)^2 - Z^2\right](e^2/2a_0)} \qquad (8)$$

The comparison between theory & experiment is...    1 Rydberg (13.6 eV)

| TWO-ELECTRON ATOM → | H⁻ | He | Li⁺ | Be²⁺ | B³⁺ | |
|---|---|---|---|---|---|---|
| $I(Z)$, Ryd. { EXPERIMENT | 0.055 | 1.807 | 5.559 | 11.311 | 19.063 | (9) |
| THIS THEORY | -0.055 | 1.695 | 5.445 | 11.195 | 18.945 | |
| % difference: EXP-THY | 200% | 6.2% | 2.1% | 1.0% | 0.6% | |

With the notable exception of H⁻, the #s agree surprisingly well (for this simple theory).

(D) **5.** The theory #s for $I(Z)$ in the table of Eq.(9) are systematically _lower_ than those calculated in Table I of Robiscoe, Am. J. Phys. **43**, 538 (1975). The reason: Robiscoe allowed for _two_ variational parameters: one for the "first" e, and one for the Hartree potential of the "second" e. The extra degree of freedom gave better agreement ✗ experiment.