On a Modified Coulomb Potential and Electronic

Correlation Energies of Simple Atoms

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A THESIS

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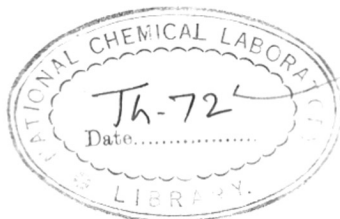
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C O N T E N T S

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LIST OF FIGURES AND TABLES

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SUMMARY

The dissertation comprises five chapters. Chapter 1 gives
a general introduction to the quantum-mechanical problem of the
spatial correlation effect in two- and many- electron atoms and
the energetic consequences thereof. A survey is made of the
various conventional approaches to the problem of electronic
correlation in atoms, such as superposition of configurations,
different orbitals for different spins, wave function containing
correlation factors and the other similar modifications of the
wave function, and their relative measures of success.

The underlying assumption of the validity of Coulomb law
for electrical point charges right upto distances on the atomic
scale, where it diverges, is manifestly stated. An a'priori
assertion is made that the physical laws of nature do not admit
such singularities and, as such, the latter must be regularised
away in any physical theory. Accordingly, the so-called corre-
lation error is attributed to the divergent character of the
Coulomb potential. An account of the possible modifications
of the Coulomb potential suggested by some workers on different
grounds is given.

Next, the significance of any departure, however small,
from the Coulombic form is brought out for the atomic fine-
structure effects (Lamb-shift) in hydrogen-like atoms,
inasmuch as the accidental degeneracy (e.g. of the

$^2S_{1/2}$ and the $^2P_{1/2}$ states), peculiar to the Coulomb potential is removed. Finally, a brief account of the variational technique and the Hartree-Fock (H-F) procedure has been comprised in for the sake of completeness and later reference.

In chapter 2 a formal derivation of the modified Coulomb potential is considered, which is based on a natural cut-off procedure. The latter takes into account the inherent quantum-mechanical uncertainty in the definition of position in the physical space. Formally, this could be interpreted as an upper cut-off for the wave-vector magnitude in the reciprocal space. This truncation procedure leads to a potential, which approaches the modified Coulomb potential of Lande' and Lande' and Thomas asymptotically for very small as well as very large distance of approach.

Chapter 3 deals with the specific problem of evaluating the ground state (spin-singlet) energies of the He- like systems (for nuclear charge number $Z = 1$ to $Z = 6$). Only one-variational-parameter wave function is used along with the modified Coulomb potential in the form

$$V(r_{ij}) = \frac{e_i e_i}{r_{ij}} (1 - e^{-\alpha_c r_{ij}}).$$

In the absence of any objective criterion known for ascertaining the precise numerical value of the cut-off parameter α_c , an estimate of it is made based on some physical reasonings.

In particular, the nuclear charge dependence of α_c is arrived at in a simple logical manner. A comparison is drawn between the ground state energy eigen-values thus obtained and those obtained from H-F method, and other variational methods using many-parameter correlated wave functions and, of course, assuming the Coulomb law. The improvement in each case is clearly indicated.

In section 2 of the chapter 3, similar calculations are carried out for the excited states (again spin-singlet states). This is accomplished by making the excited state correlated wave function orthogonal to the ground state wave functions, obtained in section 1 of the chapter 3, as well as to the energy-wise intermediate states (e.g. 1s-2s state). Energy values, thus obtained are, however, found to be much too high. It is found that independent variation of the correlated excited state wave function yields much better results.

In chapter 4 is derived an expression for the splitting of the otherwise degenerate energy levels (n $^2S_{1/2}$, n $^2P_{1/2}$) in hydrogen-like atoms. A first order perturbation calculation is made in which the Yukawa component of the modified potential has been treated as a perturbation. The validity of the 1st order perturbation calculation is discussed. The nuclear charge and the principle quantum number dependence thus obtained is shown to be in accord with the findings of Bethe based on radiative corrections. Lamb-shifts ($\Delta E(n\ ^2S_{1/2}) - \Delta E(n\ ^2P_{1/2})$) calculations on the basis of the modified Coulomb potential are shown to agree fairly well with the experimental values for the excited states of H, He (for n = 2, 3, 4) with a

suitable choice of the parameter a_c and physical basis of the choice is indicated.

Chapter 5 concludes the thesis with some reflections on the physical origin of the modifications introduced in the preceding chapter. In particular, it is observed that the modification of the Coulomb Law ($\underline{i.e.}$ $a_c < \infty$) can be adduced from the quantum-mechanical uncertainty in the definition of the relative position associated with a given pair of particles and the concommitant restriction on the extension of the reciprocal space. Thus, a plausibility of relating a_c to the reciprocal of some associated Compton length is affirmed. Some many-body theoretic aspects of the modified Coulomb law (the Yukawa term) are also analysed.

A still novel interpretation of the modified Coulomb law is conjectured in terms of a radial Markovin process, coupled with an assumed stochastic nature of the gauge invariance of the first kind.

A brief discussion of the results obtained in the precedding chapters is included.

C H A P T E R - 1

INTRODUCTION

Electronic correlation in many-electron atoms, molecules and metals (regarded as non-ideal electron gas) is a well-known kinetic effect.[1] This is caused by the Coulomb repulsion (e^2/r_{ij}) between electrons. It makes an energy contribution comparable to the self-energy of the non-interacting electron system. The largeness of the correlation effect is due, of course, to the relatively large charge-to-mass ratio of the electron. The latter is regarded as a negatively charged point mass.

The term correlation in two-and many-body systems denotes, in general, a constraint on the relative motion of the otherwise independently moving particles in the configuration space. Thus, the constraint may be purely kinematic, or purely dynamical. As an example of the former, we have the quantum-mechanical constraint of complete antisymmetry of the many-fermion wave function, due to the exclusion principle. This forbids coincidences in the configuration space. The latter comprises the spin as well as the orbital coordinates. A notable feature of such a kinematic correlation is that no corresponding term appears explicitly in the Hamiltonian of the system, and still it has non-trivial energetic consequences. It is effectively incorporated in

in the wave function through proper antisymmetrization, e.g., using Slater determinantal functions, or linear combinations thereof. It has no classical analogue.

On the other hand one has the dynamical correlation effect represented by a non-separable two-body potential term $V(r_{ij})$ occurring in the many-body Hamiltonian. The physical consequence of the non-separability of the two-body potential is to make the motion of the given particle depend explicitly on the details of motions of the rest of the particles. Thus, it is no longer possible to treat the given particle (i) in question as moving in a self-consistent one-body potential $V_{eff}(\underline{r}_i)$ obtained by averaging the two-body poentials $V(r_{ij})$ over the coordinates $(\underline{r}_j)$ of the remaining particles (j) — the so-called Hartree-Fock (H-F) procedure. In point of fact, the correlation effect is measured operationally as the difference between the exact many-body energy and the H-F energy. Thus the correlation on energy is not a physical quantity but the measure of the energy error due to the neglect of correlation in a certain approximation. It is necessarily a negative quantity. It may be noted that this spatial correlation is essentially a classical effect.

In a real quantum-mechanical many-body system the two correlation effects mentioned above co-exist. This can readily be seen for the case of a two-electron (He-like) system in the ground state. From the general variational

principle, it follows that the ground state must be orbitally nodeless (this, of course, is true of any even-fermion system) and therefore, symmetrical with respect to interchange of coordinates. Accordingly, the two spins must be aligned antiparallel to ensure overall antisymmetry, i.e. the ground state must be a spin-singlet. Thus the exclusion principle allows the two electrons to occupy the selfsame orbital state. This makes the Coulomb repulsion and, therefore, the spatial correlation effect much more pronounced for such spin-singlet states. In fact, one should expect the two electrons to avoid each other so as to create a "Coulomb hole" around each one of them. The H-F approximation, however, completely fails to correlate the electron motion for the case of antiparallel spins.

For a triplet state (parallel spins) on the other hand, the two electrons must occupy different orbital states which are orthogonal, i.e. which have minimum overlap. Thus, in effect, as a consequence of antisymmetrisation, each electron is surrounded by a 'Fermi hole'. For such spin-triplet states, therefore, much of the correlation error is automatically taken care of, even in the H-F approximation. One may say that in the H-F scheme where one uses Slater determinantal wave-function or, in other words, anti-symmetrized product wave functions comprising one-electron orbitals, an appreciable part of the correlation effect is accounted for in that each electron is surrounded by a

'Fermi hole' with respect to other electrons having the same (parallel) spin orientation. However, in the H-F scheme where some orbitals are occupied by two electrons with anti-parallel spins so as to satisfy the exclusion principle, the correlation error remains. Thus the correlation energy is usually associated with such paired electrons.

The above remarks apply generally to any two-body potential which is repulsive. Because of their mutual Coulomb repulsion two electrons try always to avoid each other to keep the energy as low as possible which leads to a certain correlation between their motions. In this connection, there is actually an increase in the kinetic energy of the two electrons because of the more complicated trajectories they have to describe, but this is compensated by a still larger decrease in the Coulomb repulsion energy; the balance is regulated by the Virial theorem,[1] $\langle T \rangle = -\frac{1}{2} \langle V \rangle$ where $\langle T \rangle$ and $\langle V \rangle$ are respectively, the quantum-mechanical expectations of the kinetic and the potential energies. (The virial theorem holds good for any bound state, i.e. the total energy of the fully relaxed system must be negative). The specific case of Coulomb potential, however, calls for special consideration inasmuch as the repulsive Coulomb interaction (e^2/r_{ij}) diverges as r_{ij} tends to zero. One may expect, therefore, the major part of the correlation energy to come from a small singular region around the electron. This will be discussed in some detail later in this chapter.

The classical work of Hylleraas[2,3,4] on the helium atom constitutes the first major contribution in the understanding of the problem of Coulomb correlation in two-electron systems. The three basic approaches proposed by him may be designated as

    (a)   Superposition of configurations

    (b)   Correlated wave functions, and

    (c)   Different orbitals for different spins.

These are briefly considered below.

(a) Method of Superposition of configurations

In this method of superposition of configurations, a complete basic set of one-electron functions $\psi_k(r_1)$ is first chosen and the space function developed in the form

$$\psi(r_1, r_2) = \sum_{kl} C_{kl} \psi_k(r_1) \psi_l(r_2),\tag{1.1}$$

with $C_{kl} = C_{lk}$. The coefficients in the expression are to be determined by the variation principle. The choice of the complete set of functions $\{\psi_k(r)\}$ to be included is not easy as the hydrogen-like functions could be used only if all the continuum states are also included. However, from a practical point of view it is convenient to restrict the set only to discrete states. According to the basic theorem, underlying the method of superposition of configurations, the set of all Ne x Ne determinants, formed by every combination of Ne one-electron functions, selected from any complete

orthonormal set, forms a complete orthonormal set over the manifold of antisymmetric Ne-electron functions. While, in principle, the basis functions are completely arbitrary so long as they constitute a complete orthonormal set, the convergence of the series expansion can be markedly improved through a proper choice of the basis.

In the actual application of the method of superposition of configurations by earlier workers one essentially makes the assumption that the basic orbitals form a complete set. The most popular basis used so far in linterature is certainly formed by the hydrogenic space-like functions together with a continuous part. The discrete subset corresponds physically to the bound states of an electron around a ~~proton~~ nucleus, whereas the continuous part corresponds to a free electron scattered by a ~~proton~~ nucleus, or semi-classically speaking, to the elliptic and hyperbolic Sommerfeld orbitals in a central field problem.

The major limitations of the method of superposition of configurations thus arise from the two subsets, discrete and continuum: (i) the discrete subset is by no means complete and (ii) the contribution of the continuum cannot be neglected in correctly expanding an arbitrary normalizable one-electron wave function in hydrogen like orbitals. Very often it is presumed on the basis of perturbation theory that the contribution of the continuum can be neglected as the corresponding functions have high orbital energies. This argument is

defective as large energy differences in the perturbation
theory denominators are offset by strong interaction matrix
elements in the numerators. In fact, several calculations
have confirmed that the contribution from the continuum is
appreciable.

Further, it is possible to simplify the resulting
matrix elements occurring in the effective Hamiltonian[1] by
choosing as the basis the ordinary and virtual Hartree-Fock
(H-F) functions, _i.e._ of the occupied or unoccupied eigen-
functions in the effective Hamiltonian

$$H_{eff}(1) = \frac{1}{2m} \underline{p}_1^2 - e^2 \sum_g \frac{z_g}{r_{1g}}$$

$$+ e^2 \int \frac{\rho(\underline{x}_2, \underline{x}_2) - \rho(\underline{x}_2, \underline{x}_1)P_{12}}{r_{12}} dx_2, \quad (1.2)$$

where $\rho(x_1, x_2)$ is the Fock-Dirac density matrix expressed
in terms of the basic set $\psi_1, \psi_2, \ldots, \psi_N$ as

$$\rho(x_1, x_2) = \sum_{k=1}^{N} \psi_k^*(x_1) \psi_k(x_2), \quad (1.3)$$

z_g is the atomic number of the nucleus at the given point g
and P_{12} is a permutation operator interchanging x_1 and x_2. This
is warranted by the Brillouin's theorem which says that all
the matrix elements for the total energy between the H-F
function and the singly excited configurations will vanish

identically.[5] Since the H-F function itself then interacts
directly only with the doubly excited configurations, the
secular equation can conveniently be solved by the perturbation
theory. Even with this approach, one has to include such H-F
functions associated with the continuum as are needed for the
completeness of the basis. The success of this approach
depends upon the possibility of evaluating the correct matrix
elements involved.

The use of projection operators[1] in the method of
superposition of configurations reveals interesting aspects
on the correlation problem. In place of the ordinary Slater
determinants, the projections of these functions are
considered as our basis. In the ordinary H-F schemes the
total wave function is approximated by a single Slater
determinant and, if the system possesses certain symmetry
properties, they may impose rather severe restrictions on
the occupied spin-orbitals. These restrictions may, however,
be removed and the total energy correspondingly decreased,
if instead the total wave function is approximated by the
 projection of a single determinant.

(b) Method of correlated wave functions

Unlike the method of superposition of configurations,
where expansions in orthogonal sets are used, the method of
correlated wave functions developed so far makes use of
expansions in power series, as originally done by Hylleraas.
For instance the Hylleraas expansion for the 1s ground state
of the helium atom is a power series in 3 variables.

$$s = r_1 + r_2, \quad u = r_{12} \quad \text{and} \quad t = -r_1 + r_2 , \qquad (1.4)$$

which can also be written in a modified form as

$$\Psi(r_1, r_2) = e^{-(1/2)s} \sum_{lmn=0} c'_{lmn} s^l u^m t^n \qquad (1.5)$$

The energy value of $E = -2.90324$ a.u. obtained by the above treatment was considered very good at the time. But the strict validity of equation (1.5) is considered questionable as this cannot be a formal solution to the Schrödinger equation.

A real progress in the use of the method of the correlated wave function is due to Kinoshita[6] who used a power series expansion in three variables

$$s, \quad p = u/s \quad \text{and} \quad q = t/u \qquad (1.6)$$

which are independent of one another and have the domains $(0, \infty), (0, 1)$ and $(-1, 1)$, respectively. Because of the identity

$$s^l p^m q^n = s^{l-m} u^{m-n} t^n , \qquad (1.7)$$

such a power series corresponds to an expansion in s, u, t of the form

$$\Psi(r_1, r_2) = e^{-(1/2)s} \sum_{l, m, n=0} c_{lmn} s^{l-m} u^{m-n} t^n . \qquad (1.8)$$

According to Kinoshita such a series could be a formal
solution of the Schrödinger equation. Using a 39-term
function, Konishita obtained the energy value
E = - 2.9037225 a.u. This is in good agreement with the
experimental value .

Using a very similar set of three variables

$$s, \qquad \zeta = u/s \qquad \text{and} \qquad \gamma = -t/s \qquad (1.9)$$

having the ranges (0, ∞), (0, 1) and (-1, ζ),
respectively Pluvinage[7] obtained an even better energy
eigenvalue

$$E = - 2.903892 \text{ a.u.}$$

It may be noted that Kinoshita does not consider the inclu-
sion of logarithmic terms in the expansion as a necessary
requirement of the Schrödinger equation.

Though a correlated wave function of the type (1.5)
or (1.10) is found to yield a value of high accuracy for the energy
eigenvalue for the helium atom, it cannot be said to reveal
the actual form of the corresponding eigenfunction. Thus
neither the correlated wave functions nor the superposition
of configurations can reveal the characteristics of the
wave functions if these methods are to depend on the variation
principle. Hence, the correlated wave functions of the type
(1.5) or (1.10) for helium has not the same high degree of

of physical visuality as is characteristic for the simple
wave function $(1s)^2$ in the one-electron scheme. It is
therefore, of interest to study whether the correlation
effects could be introduced in the latter simpler way, e.g.
in the form of "correlation factor" $g(r_{12})$ containing the
interelectronic distance r_{12}, such as

$$\Psi(r_1, r_2, r_{12}) = u(r_1)\, u(r_2)\, g(r_{12}). \qquad (1.11)$$

The incidence of such correlation factor in the wave
function can be justified from the consideration of the
asymptotic form of the wave function.[8]

This approach was also first sketched by Hylleraas
himself. He pointed out that by choosing $u = 1s$ and
$g = e^{ar_{12}}$, one could obtain the surprisingly good energy
$E_{He} = -2.8896$ a.u. He also showed that by choosing the
very simple correlation factor $g = 1 + ar_{12}$, one could reach
the still better energy value $E_{He} = -2.8912$ a.u.

Löwdin and Rédei[9] have used a wave function of the
type $u^2(1+ar_{12})$, where u is expressed either as a single
exponential or as the sum of two exponentials:

$$u = (\, A_1\, e^{-a_1 r} + A_2\, e^{-a_2 r}\,) \qquad (1.12)$$

The function (1.11) with more general forms of the functions
u and g has also been studied in greater detail by Baber

and Hasse[10] and by Pluvinage.[11] The latter expanded $g(r_{12})$ in a power series in r_{12} and by studying the formal properties of the wave equation itself, he could derive certain general relations for the coefficients. According to Roothaan[12] by expressing u and g in the form

$$u(r) = e^{-\eta r} \sum_{n=0,2} a_n r^n$$

$$g(r_{12}) = 1 - e^{-\alpha r_{12}} \sum_{m=0,3} b_m r^m$$

$$(1.12)$$

and minimizing all parameters, it is possible to reach an energy minimum of

$$E_{He} = -2.90036 \text{ a.u.}$$

It is of interest to note that the correlation factor can be combined with the method of superposition of configurations. By such a combination of the two methods it is possible to obtain any accuracy desired by means of comparatively simple wave functions.[9] For a very general class of functions $g(r_{12})$, the quotient $\Psi(x_1,x_2) / g(r_{12})$ is written as the products of one-electron functions $\Psi_k(r)$, which leads to the desired expansion

$$\Psi(x_1,x_2) = g(r_{12}) \sum_{kl} C_{kl} \Psi_k(r_1) \Psi_l(r_2),$$

$$(1.14)$$

where $C_{kl} = C_{lk}$.

(c) Method of different orbitals for different spins

The large correlation errors in the conventional H-F approximation certainly depends on the fact that pairs of electrons of opposite spins are forced together in doubly filled orbitals. This pairing is admitted on the classical formulation of the Pauli principle, and further as it permits a simple constitution of pure spin states. It is therefore of interest to examine if one could remove at least part of the defects coming from correlation by, as first suggested by Hylleraas[4] and by Eckart[13] letting electrons with different spins occupy different orbitals in space so that they get a chance to avoid each other in accordance with the influence of the Coulomb repulsion.

A generalization of the idea of 'different orbitals for different spins' is hence possible, only by explicit treatment of the connected spin problem. It is clear that, if one permits "different orbitals" for different spins, the corresponding Slater determinant will no longer be pure spin functions but mixtures of components associated with different spins. The total wave function will be thus approximated by the component of the Slater determinant which has the spin desired. Such components of a given spin multiplicity can be projected out by a projection operator as given by Löwdin.[14]

Recently it has been pointed out by Slater[15] that in a system with unbalanced spins having, $s_g \neq 0$, the

electrons with plus spin would be influenced by an exchange
potential other than the electrons with negative spin, since
the exchange interactions occur only between the electrons
having parallel spins. It is, therefore, expected that
electrons with different spins would have different orbitals.

In the so-called unrestricted H-F scheme developed
by Slater and collaborators[8,11] for treating the exchange
polarization, the total wave function is approximated by a
single determinant where electrons with different spins may
have different orbitals. The H-F equations become parti-
cularly simple, since there are no non-diagonal multipliers
but the total wave function does not usually represent a
pure spin state. Pratt[16] has examined the validity of this
approach by considering the $(1S)^2(2S)$ ground state of the
Li atom. His results show that the total energy of the
lowest state actually decreases when going from the conven-
tional to the unrestricted H-F scheme.

Thus the method of using 'different orbitals for
different spins' constitutes a definite advancement of the
entire frame-work of the independent-particle model. There
seems to be essential physical reasons for a compara-
tively large orbital splitting depending on correlation,
since electrons with opposite spins try to avoid each other
because of their mutual Coulomb repulsion, and, in systems
with unbalanced spins, there may further exist an extra
exchange polarization of the type emphasized by Slater.

It may well be noted at this juncture that the above treatments are all based on implicit assumption of the validity of the Coulomb law for small distances of approach, even on the atomic scale when the potential tends to diverge. As it is the contention of the present dissertation that much of the correlation error is due to the unphysical nature of this divergence, it may be in order to review briefly various suggestions that have been made from time to time regarding the possible modifications of the Coulomb law at small distances of approach so as to remove the singularity. This question of Coulomb singularity is intimately connected with the classical problem of infinite self-energy of a point charge and has, as such, attracted the attention of many. The idea of ascribing a small but non-zero (classical) radius to the electron so as to envisage a finite extended region of impenetrability had to be abandoned as the latter was shown by Poincaré[17] to be essential conflict with the requirements of special relatively.

Earlier attempts on the classical level at removing the problem of infinite self-energy of an ideal point charge (Lorentz model) include the suggestions of Born and Infeld,[18] Born,[19] Bopp[20] and Wheeler and Feynman.[21]

Born and Infeld[18] proposed a non-linear modification of Maxwell's theory to get rid of the infinity. This, however, leads to a number of unphysical predictions regarding self-force (Bootstrap force).   Dirac has made an interesting

suggestion in which electron acted upon itself through only half retarded minus half advanced potentials. In this way, the electron turned out to have the right radiation resistance while the divergent terms in the expression for the self-force cancelled out exactly.

Wheeler and Feynman[21] proposed a theory based on the original suggestion of Fränkel that the electron acted only on other electrons (Fränkel field concept), and that too via half retarded plus half advanced potentials. The above idea together with a supposition of the universal radiation absorber surrounding the system in question gave finite results. In fact, there was no self-energy at all. Later the idea of field was completely abandoned and replaced by that of retarded action-at-a-distance. The equality of action and reaction was, of course, retained.

A novel modification of the laws of electrodynamics was suggested by Bopp.[20] This was based on a possible modification of the relativistic laws of communication according to which all electromagnetic interactions take place on the light cone, i.e. the fundamental interval.

$$ds^2 = c^2 dt^2 - dx^2 - dy^2 - dz^2 = 0. \tag{1.15}$$

It was postulated that the interaction is communicated off the light cone as well as on a "liberation"

$$ds^2 = c^2 dt^2 - dx^2 - dy^2 - dz^2 \leq a^2, \tag{1.16}$$

where 'a' is a width parameter. This was shown to lead
to the modified Coulomb law in the form

$$V(r_{ij}) = \frac{e_i e_i}{r_{ij}} (1 - e^{-r_{ij}/a}) . \tag{1.17}$$

This, of course, reduces to the usual Coulomb law for 'a'
tending to zero. As can easily be seen, the above expression
tends to a finite value $e_i e_j/a$ for r_{ij} tending to zero.

Landé[22] and Landé and Thomas[23] tried to resolve the
divergence difficulty by suggesting a modified form for the
Coulomb law on semi-classical grounds by taking into account
radiative damping of each Fourier component appearing in the
Fermi's representation of classical electromagnetic field.
The same form was obtained by Podolsky[24] through a generali-
sation of the lagrangian of the electro-magnetic field with
charge particles so as to include the second derivative of
the field quantities. This led to a generalised Poisson
equation,

$$(1 - \lambda^2 \nabla^2) \nabla^2 \phi = - 4\pi \rho , \tag{1.18}$$

where ϕ is the scalar potential, ρ the point charge
density ($\rho = e\delta(r)$, where $\delta(r)$ is the Dirac delta function)
and 'λ' is a parameter having the dimension of length but
completely arbitrary otherwise. The only acceptable solution
is

$$\phi(r) = e/r (1 - e^{-r/\lambda}). \tag{1.19}$$
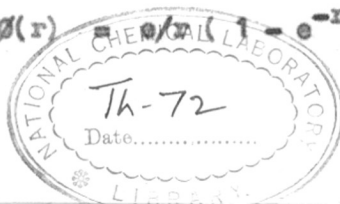
As can be easily seen $\emptyset(r)$ tends to a finite value e/λ for r tending to zero, and hence finite self-energy of a point charge.

The modifications of Maxwell's equation (Coulomb law) mentioned above are all classical in nature. So far no satisfactory quantum theory has been developed. It has been found that the classical divergence is by no means removed when the field is quantised. In fact, the problem of divergence for the electron radius tending to zero is replaced by the problem of infinite energy with the reciprocal-space vector cut-off tending to infinity.

Whatever mathematical basis may be for the modifications of the Coulomb law, a deviation from the latter would lead to one directly observed effect, viz. the atomic fine structure or Lamb-Shift. As is well known, the pure Coulomb potential leads to accidental degeneracy for one-electron hydrogen-like atoms. Thus the atomic states such as $2\,^2S_{1/2}$ and $2\,^2P_{1/2}$ are degenerate not only for the Schrödinger Hamiltonian but also in the Dirac theory. This is in contradiction with experimental results and a great deal of theoretical work has been done to explain the level shift in terms of corrections involving virtual photon processes. On the other hand a deviation from the Coulomb-law, however small, will necessarily lead to the removal of such accidental degeneracies. This may provide a natural, though phenomenological, explanation of Lamb-shift.

C H A P T E R - 2

REFORMULATION OF THE MODIFIED COULOMB POTENTIAL

We consider a formal deviation of a modified Coulomb
potential, which is based on a natural cut-off procedure. The
latter takes into account the inherent quantum-mechanical
uncertainty in the definition of position in the physical
space. Thus, it is meaningless to speak of distances smaller
than a characteristic length of the order of the Compton
wave length for a given particle. Formally, this can be
interpreted as an upper cut-off for the wave-vector magnitude
in the reciprocal space. Thus in the Fourier expansion of
the Coulomb potential, namely,

$$\frac{e_i e_j}{r_{ij}} = \sum_{k=0}^{\infty} \frac{4\pi e_i e_j}{\Omega\, k^2} e^{i\underline{k}\cdot\underline{r}_{ij}} , \qquad (2.1)$$

where Ω is the normalisation volume and $\underline{k}$ is reciprocal
space vector, the summation has to be truncated at an appro-
priate upper cut-off, say k_c. Accordingly, we define a
modified Coulomb law as

$$V(r_{ij})_{truncated} = \sum_{k=0}^{|\underline{k}| = k_c} \frac{4\pi e_i e_j}{\Omega\, k^2} e^{i\underline{k}\cdot\underline{r}_{ij}} . \qquad (2.2)$$

Incidentally, the truncation procedure adopted here,
which involves Fourier expansion in terms of orthogonal sets,

ensures the minimal deviation from the unmodified Coulomb law
in the standard least square sense. Changing summation over k
to 'integration in (2.2), we get

$$V(r_{ij})_{truncated} = e_i e_j \; \frac{2}{\pi} \; \frac{1}{r_{ij}} \; S_i(k_c \, r_{ij}), \qquad (2.3)$$

where

$$S_i(x) = \int_0^x \frac{\sin y}{y} \, dy .$$

In fact, in the path integral approach of Feynman the
Coulomb law of interaction between two point charges is arrived
at by integrating out the longitudinal photon coordinates. Here
again by using a wave vector cut-off for the longitudinal
photons, it can easily be shown that one gets a modified
Coulomb law identical with (2.3)

It can readily be seen that the asymptotic form of (2.3)
in the limit $k_c r_{ij} \ll 1$ as well as $k_c r_{ij} \gg 1$ is
essentially the same as of that given in (1.19) for the choice
$k_c = \frac{\pi}{2} \frac{1}{\lambda}$. For the intermediate values (i.e. $k_c r_{ij} \sim 1$),
however, the two potentials differ in some measure, namely,
while (1.19) tends to coulombic form aperiodically for r_{ij}
increasing, the truncated potential oscillates about the
coulombic values in a damped fashion. Mathematically, this
reflects the sharp wave-vector cut-off employed here in
contradistinction with the tapered cut-off procedure used by
Landé and Thomas. The plot in fig.1 displays the above
behaviour graphically. Ofcourse, in the region of interest,

i.e. $k_c r_{ij} \ll 1$, there is nothing much to choose between the two forms. For analytical simplicity, a modified potential $V_m(r_{ij})$ in the form

$$V_m(r_{ij}) = \frac{e_i e_j}{r_{ij}} (1 - e^{-a_c r_{ij}}), \text{ with } a_c = 1/\lambda_c \qquad (2.4)$$

will be actually employed in subsequent computations. It may be noticed from the fig.1 that, in the mean, the present potential (cf (2.3)) converges more rapidly to the coulombic form than that given in (1.19). The Fourier transform of (2.4) is, of course,

$$4\pi e_i e_j (\frac{1}{k^2} - \frac{1}{k^2 + k_c^2}). \qquad (2.5)$$

Aside from a factor $\frac{1}{2}$ in the second term of (2.5), this is exactly the same result as that obtained by Hubbard[25] for the treatment of the correlation problem in electron gas with, $a_c = k_F$, where k_F is Fermi wave-vector magnitude. The factor $\frac{1}{2}$ appears in his case as only the interaction between electrons of opposite spins was considered. Thus, there seems to be strong indication that the modified potential should be of the form given in (2.4). It will be shown in the following chapters that it accounts for the residual correlation error and also removes the accidental degeneracy associated with the pure Coulomb law, and thus provides a natural explanation of some atomic fine-structure effects (e.g. Lamb-shift).
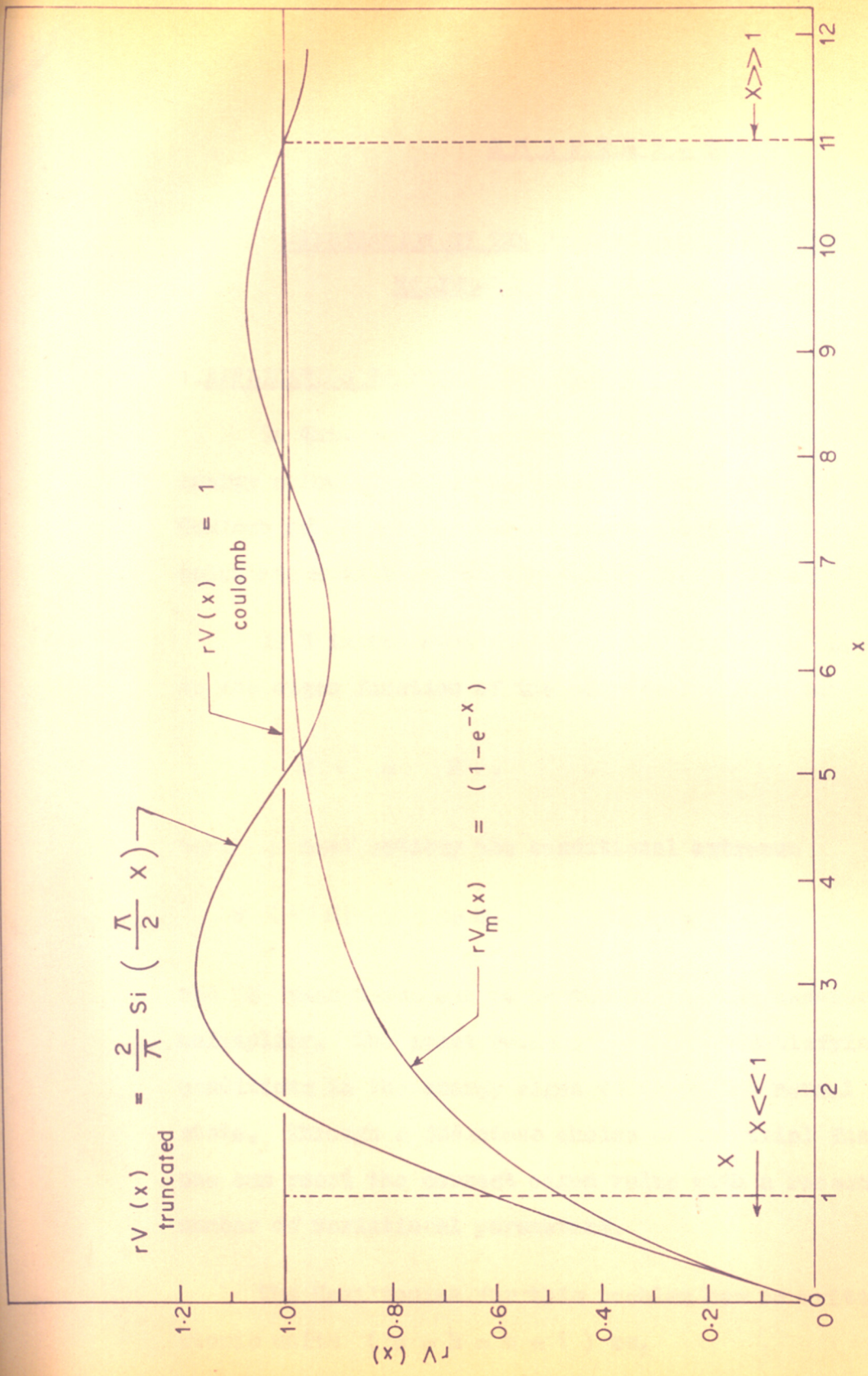
FIG. 1. COMPARISON OF THE COULOMB, THE MODIFIED AND THE TRUNCATED TWO-BODY POTENTIALS, PLOTTED AS FUNCTIONS OF THE DIMENSIONLESS VARIABLE $x = \alpha_c r$

C H A P T E R - 3

APPLICATION OF THE MODIFIED COULOMB POTENTIAL TO
HELIUM-LIKE TWO-ELECTRON ATOMS

1. APPLICATION TO THE GROUND STATE

In this chapter, we shall discuss the ground state
energy calculation of the He-like atoms using the modified
Coulomb potential for the electron-electron interaction. The
calculation is based on the well known variational principle.[26]

If H is the Hamiltonian of the system in question and ψ
is the eigen function of the Schrodinger equation

$$H \psi = E \psi, \tag{3.1}$$

then ψ must satisfy the conditional extremum

$$\delta \langle \psi | H | \psi \rangle = 0, \qquad \langle \psi | \psi \rangle = 1 \tag{3.2}$$

and E then turns out to be the Lagrangian undetermined
multiplier. The least value of $\langle \psi | H | \psi \rangle$ satisfying the above
conditions is the energy eigen value of the normal (ground)
state. Through a judicious choice of the trial function ψ,
one can reach the correct eigen value with a reasonably small
number of variational parameters.

The Hamiltonian for this problem can be written in
atomic units ($e = \hbar = m = 1$) as,

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}}(1 - e^{-\alpha_r r_{12}}), \tag{3.3}$$

where ∇_i^2 is the Laplacian for the ith electron and is given by

$$\nabla_1^2 \Psi = \frac{\partial^2 \Psi}{\partial x_1^2} + \frac{\partial^2 \Psi}{\partial y_1^2} + \frac{\partial^2 \Psi}{\partial z_1^2}, \tag{3.4}$$

where

$$\Psi = \Psi(x_1, y_1, z_1; x_2, y_2, z_2)$$

$$= \Psi(r_1, r_2, r_{12}) \tag{3.5}$$

is the total wave function .

$$\frac{\partial^2 \Psi}{\partial x_1^2} = \frac{\partial^2 \Psi}{\partial r_1^2}\frac{x_1^2}{r_1^2} + \frac{\partial \Psi}{\partial r_1}\left(\frac{1}{r_1} - \frac{x_1^2}{r_1^3}\right) + \frac{\partial^2 \Psi}{\partial r_{12}^2}\frac{(x_1-x_2)^2}{r_{12}^2}$$

$$+ \frac{\partial \Psi}{\partial r_{12}}\left[\frac{1}{r_{12}} - \frac{(x_1-x_2)^2}{r_{12}^3}\right] + 2\frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}}\frac{(x_1-x_2)}{r_1 r_{12}}. \tag{3.6}$$

Adding the similar terms for $\frac{\partial^2 \Psi}{\partial y_1^2}$ and $\frac{\partial^2 \Psi}{\partial z_1^2}$, we get $\nabla_1^2 \Psi$ in bi-polar coordinates as,

$$\nabla_1^2 \Psi = \frac{\partial^2 \Psi}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial \Psi}{\partial r_1} + \frac{\partial^2 \Psi}{\partial r_{12}^2} + \frac{2}{r_{12}}\frac{\partial \Psi}{\partial r_{12}} +$$

$$+ \frac{1}{r_1 r_{12}}\frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}}\left[r_{12}^2 + r_1^2 - r_2^2\right], \tag{3.7}$$

with a similar expression for $\nabla_2^2 \psi$. Thus

$$\nabla_1^2 \psi + \nabla_2^2 \psi = \frac{\partial^2 \psi}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial \psi}{\partial r_1} + \frac{\partial^2 \psi}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial \psi}{\partial r_2}$$

$$+ \frac{2}{r_{12}}\frac{\partial^2 \psi}{\partial r_{12}^2} + \frac{4}{r_{12}}\frac{\partial \psi}{\partial r_{12}} + \frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}}\frac{\partial^2 \psi}{\partial r_1 \partial r_{12}}$$

$$+ \frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}}\frac{\partial^2 \psi}{\partial r_2 \partial r_{12}} \tag{3.8}$$

For calculating the ground state energy with the Hamiltonian (3.3), we use the variational procedure. We choose a product wave function of one-electron hydrogen like 1s orbitals along with a correlation factor $g(r_{12})$, namely,

$$\psi(\underline{r}_1, \underline{r}_2, \underline{r}_{12}) = u(\underline{r}_1)\, u(\underline{r}_2)\, g(\underline{r}_{12}) / N^{1/2}, \tag{3.9}$$

where

$$u(\underline{r}) = (\frac{z^3}{\pi})^{1/2} e^{-zr}, \tag{3.10}$$

$$g(r_{12}) = (1 + \beta r_{12}). \tag{3.11}$$

Here β is a variational parameter.

N is determined by the normalization constraint,

$$\int \psi \psi^* \, d\tau = 1, \tag{3.12}$$

where

$$d\tau = r_1 dr_1 \ r_2 dr_2 \ r_{12} dr_{12} \ \sin\Theta. \ d\Theta. \ d\chi$$

$$= 8\pi^2 r_1 dr_1 \ r_2 dr_2 \ r_{12} dr_{12}$$

The integral $\int \psi^2 d\tau$ becomes

$$\int \psi^2 d\tau = \frac{Z^6}{\pi^2} \frac{8\pi^2}{N} \iiint r_1 e^{-2zr_1} r_2 e^{-2zr_2} x$$

$$x \ (1 + \beta r_{12}) r_{12} dr_1 dr_2 dr_{12} \qquad\qquad (3.13)$$

The ranges of the integration are

$$0 \le r_1 \le \infty, \quad 0 \le r_2 \le \infty \ ; \quad |r_2 - r_1| \le r_{12} \le r_1 + r_2.$$

The absolute value sign on the limit for r_{12} splits the integration over r_2 into two parts, (a) $r_2 \langle r_1$, (b) $r_2 \rangle r_1$. In range (a) the lower limit of r_{12} is $r_2 - r_1$, in case of (b) it is $r_1 - r_2$. Thus

$$\int \psi^2 d\tau = \frac{8z^6}{N} \int_0^\infty r_1 e^{-2zr_1} dr_1 \int_{r_1}^\infty r_2 e^{-2zr_2} dr_2 \int_{r_2-r_1}^{r_2+r_1} (1+\beta r_{12})^2 r_{12} dr_{12}$$

$$+ \int_0^\infty r_2 e^{-2zr_2} dr_2 \int_{r_2}^\infty r_1 e^{-2zr_1} dr_1 \int_{r_1-r_2}^{r_1+r_2} (1+\beta r_{12})^2 r_{12} dr_{12}.$$

$$\cdots\cdots(3.14)$$

Inspection shows that the two triple integrals are equal. Hence

$$\int \psi^2 d\tau = \frac{16z^6}{N} \int_0^\infty e^{-2zr_1} r_1 dr_1 \int_{r_1}^\infty e^{-2zr_2} r_2 dr_2 \int_{r_2-r_1}^{r_2+r_1} (1+\beta r_{12})^2 r_{12} dr_{12}$$

$$= \frac{1}{N} \left[1 + \frac{35}{8z} \beta + \frac{6\beta^2}{z^2} \right] \qquad (3.15)$$

From (3.12) we get the value of N

$$N = \left[1 + \frac{35}{8z} \beta + \frac{6}{z^2} \beta^2 \right]. \qquad (3.16)$$

Next we calculate $\nabla_1^2 \psi + \nabla_2^2 \psi$ as follows:

On using the wave function (3.9) we get,

$$\frac{\partial \psi}{\partial r_1} = \frac{\partial \psi}{\partial r_2} = \frac{-z^4}{\pi \sqrt{N}} e^{-zr_1} e^{-zr_2}(1+\beta r_{12}), \qquad (3.17)$$

$$\frac{\partial^2 \psi}{\partial r_1^2} = \frac{\partial^2 \psi}{\partial r_2^2} = \frac{z^5}{\pi \sqrt{N}} e^{-zr_1} e^{-zr_2} (1+\beta r_{12}), \qquad (3.18)$$

$$\frac{\partial \psi}{\partial r_{12}} = \frac{z^3 \beta}{\pi \sqrt{N}} e^{-zr_1} e^{-zr_2} , \qquad (3.19)$$

$$\frac{\partial^2 \psi}{\partial r_{12}^2} = 0 , \qquad (3.20)$$

$$\frac{\partial^2 \psi}{\partial r_1 \partial r_{12}} = \frac{\partial^2 \psi}{r_2 r_{12}} = \frac{z^3 \beta}{\pi \sqrt{N}} e^{-zr_1} e^{-zr_2} . \tag{3.21}$$

Hence from (3.8) we get,

$$\nabla_1^2 \psi + \nabla_2^2 \psi = \frac{z^3}{\pi \sqrt{N}} \left\{ \left[2z^2 - 2(\frac{1}{r_1} + \frac{1}{r_2})z \right] (1+\beta r_{12}) + \right.$$

$$\left. + \frac{4}{r_{12}} \beta - \frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}} \beta z - \frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \beta z \right\} \times$$

$$x \ e^{-zr_1} e^{-zr_2} . \tag{3.22}$$

Now the Hamiltonian (3.3) is given by

$$H\psi = \frac{z^3}{\pi \sqrt{N}} \left[-z^2(1+\beta r_{12}) + \frac{\beta z}{2} r_{12} (\frac{1}{r_1} + \frac{1}{r_2}) - \frac{2\beta}{r_{12}} + \right.$$

$$+ \frac{r_1^2 r_2 - r_2^3 + r_2^2 r_1 - r_1^3}{2 \ r_1 r_2 r_{12}} \beta z +$$

$$\left. + \frac{1}{r_{12}} (1+\beta r_{12})(1 - e^{-\alpha_c r_{12}}) \right] x \ e^{-zr_1} e^{-zr_2} \tag{3.23}$$

Using the wave function (3.9) and the Hamiltonian (3.23)
the energy expectation value $E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$
is calculated as follows:

$$E = I_1 + I_2 + I_3 + I_4 + I_5 , \tag{3.24}$$

where

$$L_1 = \frac{-Z^2 N \int \psi \psi^* \, d\tau}{N \int \psi \psi^* \, d\tau} = -Z^2 , \tag{3.25}$$

$$I_2 = \frac{16Z^6}{N} \int_0^\infty \frac{\beta Z}{2} e^{-2zr_1} r_1 dr_1 \int_{r_1}^\infty \left(\frac{1}{r_1} + \frac{1}{r_2}\right) r_2 \, e^{-2zr_2} dr_2 \ \times$$

$$x \int_{r_2-r_1}^{r_2+r_1} r_{12}(1+\beta r_{12}) r_{12} dr_{12}$$

$$= -\frac{1}{N} \left[\frac{15}{8} \beta Z + \frac{9}{2} \beta^2 \right], \tag{3.26}$$

$$I_3 = -16 \frac{1}{Z} Z^6 \beta \int_0^\infty 2r_1 e^{-2zr_1} dr_1 \int_{r_1}^\infty e^{-2zr_2} r_2 dr_2 \ \times$$

$$x \int_{r_2-r_1}^{r_2+r_1} (1+\beta r_{12}) dr_{12}$$

$$= \frac{-1}{N} \left[\frac{5}{4} \beta Z + 2\beta^2 \right], \tag{3.27}$$

$$I_4 = \frac{16}{2} \times \frac{1}{N} z^6 \beta z \int_0^\infty e^{-2zr_1} dr_1 \int_{r_1}^\infty (r_1^2 r_2 - r_2^3 + r_2^2 r_1 - r_1^3) e^{-2zr_2} dr_2 \times$$

$$\times \int_{4_2 - r_1}^{r_2 + r_1} (1 + \beta r_{12}) dr_{12}$$

$$= - \frac{1}{N} \left[\frac{5}{8} \beta z + \frac{3}{2} \beta^2 \right] , \tag{3.28}$$

$$I_5 = 16 \frac{1}{N} z^6 \int_0^\infty e^{-2zr_1} r_1 dr_1 \int_{r_1}^\infty e^{-2zr_2} r_2 dr_2 \times$$

$$\times \int_{r_2 - r_1}^{r_2 + r_1} (1 + \beta r_{12})^2 (1 - e^{-\alpha} e^{r_{12}}) dr_{12}$$

$$I_5 = I_{5.1} + I_{5.2} , \tag{3.29}$$

where

$$I_{5.1} = \frac{16}{N} z^6 \int_0^\infty e^{-2zr_1} r_1 dr_1 \int_{r_1}^\infty e^{-2zr_2} r_2 dr_2$$

$$\int_{r_1 - r_1}^{r_2 + r_1} (1 + \beta r_{12})^2 dr_{12}$$

$$= \frac{1}{N} \left[\frac{5}{8} z + 2\beta + \frac{35}{16} \frac{\beta^2}{z} \right] , \tag{3.30}$$

and

$$I_{5.2} = -16 \frac{1}{N} Z^6 \int_o^\infty e^{-2zr_1} r_1 dr_1 \int_{r_1}^\infty e^{-2zr_2} r_2 dr_2 \quad \times$$

$$\times \int_{r_2-r_1}^{r_2+r_1} e^{-\alpha_c r_{12}} (1+2\beta r_{12}+\beta^2 r_{12}^2) dr_{12}$$

$$I_{5.2} = -\frac{16}{N} \frac{Z^6}{\alpha_c} \left[\frac{1+2\beta}{\alpha_c} + \frac{2\beta^2}{\alpha_c^2} \right]\left[\frac{1}{32Z^3(\alpha_c+2Z)} + \frac{1}{16Z^2(\alpha_c+2Z)^2} \right.$$

$$\left. - \frac{1}{2(\alpha_c+2Z)^4} \right] - \frac{32Z^6\beta}{N\alpha_c} \left[1 + \frac{\beta}{\alpha_c} \right] \times$$

$$\times \left[\frac{1}{32Z^3(\alpha_c+2Z)^2} + \frac{1}{8Z^2(\alpha_c+2Z)^3} - \frac{2}{(\alpha_c+2Z)^5} \right]$$

$$- \frac{16Z^6\beta^2}{N\alpha_c} \left[\frac{1}{16Z^3(\alpha_c+2Z)^3} + \frac{3}{8Z^2(\alpha_c+2Z)^4} - \frac{10}{(\alpha_c+2Z)^6} \right].$$

$$\ldots\ldots(3.31)$$

The energy expression (3.24) is

$$E = -Z^2 + \left(\frac{1}{N} \right) (A + B\beta + C\beta^2), \qquad (3.32)$$

where

$$A = \frac{5}{8} Z - \frac{16Z^6}{\alpha_c} D_1 , \qquad (3.33)$$

$$B = 2 - \frac{32Z^6}{a_c^2} D_I - \frac{32Z^6}{a_c} D_{II} , \qquad (3.34)$$

$$C = 1 + \frac{35}{16Z} - \frac{32Z^6}{a_c^3} D_I - \frac{32Z^6}{a_c^2} D_{II} - \frac{16Z^6}{a_c} D_{III}, \qquad (3.35)$$

with

$$D_I = \frac{1}{32Z^3(a_c + 2Z)} + \frac{1}{16Z^2(a_c + 2Z)^2} - \frac{1}{2(a_c + 2Z)^4} , \qquad (3.36)$$

$$D_{II} = \frac{1}{32Z^3(a_c + 2Z)^2} + \frac{1}{8Z^2(a_c + 2Z)^3} - \frac{2}{(a_c + 2Z)^5} , \qquad (3.37)$$

$$D_{III} = \frac{1}{16Z^3(a_c + 2Z)^3} + \frac{3}{8Z^2(a_c + 2Z)^4} - \frac{10}{(a_c + 2Z)^6} . \qquad (3.38)$$

The minimization of the energy function with respect to β

$$\frac{\partial E}{\partial \beta} = 0 \qquad \text{gives}$$

$$(B + 2\beta C)\left[1 + \frac{35}{8Z}\beta + \frac{6}{Z^2}\beta^2\right] - [A + B\beta + C\beta^2]\left[\frac{35}{8Z} + \frac{2 \times 6\beta}{Z^2}\right] = 0 \qquad (3.39)$$

that is ,

$$\left[B - \frac{35}{8Z}A\right] + \left[\frac{35}{8Z}B + 2C - \frac{35}{8Z}B - \frac{12A}{Z^2}\right]\beta + \left[\frac{6B}{Z^2} + \frac{2 \times 35}{8Z}C - \frac{12}{Z^2}B\right]\beta^2 +$$

$$+ \left[\frac{12C\beta^3}{Z^2} - \frac{12C\beta^3}{Z^2}\right] = 0 \qquad (3.40)$$

i.e.

$$[B - \frac{35}{8Z}A] + (2C - \frac{12A}{Z^2})\beta + [\frac{35C}{8Z} - \frac{6B}{Z^2}]\beta^2 = 0, \qquad (3.41)$$

where

$$[B - \frac{35A}{8Z}] = (2 - \frac{32Z^6}{\alpha_c^2} D_I - \frac{32Z^6}{\alpha_c} D_{II}) - \frac{35}{8Z}(\frac{5}{8}Z - \frac{16Z^6}{\alpha_c} D_I)$$

$$= 2 - \frac{35 \times 5}{64} + (-\frac{32Z^6}{\alpha_c^2} + \frac{70Z^5}{\alpha_c})D_I - \frac{32Z^6}{\alpha_c} D_{II}$$

$$= -\frac{47}{64} + (\frac{70Z^5}{\alpha_c} - \frac{32Z^6}{\alpha_c^2})D_I - \frac{32Z^6}{\alpha_c}D_{II}, \qquad (3.42)$$

$$[2C - \frac{12A}{Z^2}] = 2[1 + \frac{35}{16}\frac{1}{Z} - \frac{32}{\alpha_c^3}Z^6 D_I - \frac{32Z^6}{\alpha_c^2} D_{II} - \frac{16Z^6}{\alpha_c}D_{III}]$$

$$- \frac{12}{Z^2}[\frac{5}{8}Z - \frac{16Z^6}{\alpha_c}D_I]$$

$$= 2 - \frac{25}{8Z} + (\frac{192Z^4}{\alpha_c} - \frac{64Z^6}{\alpha_c^3}) - \frac{64Z^6}{\alpha_c^2}D_{II} - \frac{32Z^6}{\alpha_c}D_{III},$$

$$\qquad \qquad \cdots\cdots (3.43)$$

and

$$[\frac{35C}{8Z} - \frac{6B}{Z^2}] = \frac{35}{8Z}[1 + \frac{35}{16}\frac{1}{Z} - \frac{32Z^6}{\alpha_c^3}D_I - \frac{32Z^6}{\alpha_c^2}D_{II} - \frac{16Z^6}{\alpha_c}D_{III}]$$

$$- \frac{6}{Z^2}[2 - \frac{32Z^6}{\alpha_c^2}D_I - \frac{32Z^6}{\alpha_c}D_{II}]$$

$$= \frac{35}{8Z} + (\frac{(35)^2}{128} - 12)\frac{1}{Z^2} + (\frac{192Z^4}{\alpha_c^2} - \frac{140Z^5}{\alpha_c^3})D_I$$

$$+ (\frac{192Z^4}{\alpha_c} - \frac{140Z^5}{\alpha_c^2})D_{II} - \frac{70Z^5}{\alpha_c}D_{III}. \qquad (3.44)$$

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Equations (3.41) to (3.44) give the relation for the minimization of the energy with respect to β as:

$$\beta^2 \left[\frac{35}{8Z} + \left(\frac{(35)^2}{128} - 12 \right) \frac{1}{Z^2} + \left(\frac{192Z^4}{\alpha_c^2} - \frac{140Z^5}{\alpha_c^3} \right) D_I \right.$$

$$\left. + \left(\frac{192Z^4}{\alpha_c} - \frac{140Z^5}{\alpha_c^2} \right) D_{II} - \frac{70Z^5}{\alpha_c} D_{III} \right]$$

$$+ \beta \left[2 - \frac{25}{8Z} + \left(\frac{192Z^4}{\alpha_c} - \frac{64Z^6}{\alpha_c^2} \right) D_I - \frac{64Z^6}{\alpha_c^2} D_{II} - \frac{32Z^6}{\alpha_c} D_{III} \right]$$

$$+ \left[-\frac{47}{64} + \left(\frac{70Z^5}{\alpha_c} - \frac{32Z^6}{\alpha_c^2} \right) D_I - \frac{32Z^6}{\alpha_c} D_{II} \right] = 0 \qquad (3.45)$$

The justification for the occurrence of a correlation factor of the type $g(r_{12})$ in many electron functions has been given by several authors from considerations of the asymptotic form of the wave functions.[8] We shall show that with a single variational parameter β, we get very much improved agreement between calculated and exact energy values for the helium series for $Z = 1$ to $Z = 6$.

It should be noted that the choice of α_c still remains arbitrary. We shall be guided by some physical reasoning. In the correlation problem of metals the screening length is of the order of Bohr radius.[27] The Bohr radius for hydrogen like system is given by $a_0 = \frac{\hbar^2}{me^2}$. Inasmuch

as α_c is the reciprocal of a characteristic length of the order of atomic dimension, we choose α_c in atomic units as

$$\alpha_c = \alpha_o \, f(Z), \qquad\qquad (3.46)$$

where α_o is the reciprocal of Bohr radius, and $f(Z)$ is some function of Z. The dependence of α_c on the nuclear charge Z can be seen to follow from the following reason. As Z increases, it will increasingly mask the effect of repulsive interaction between two electrons thereby allowing them to come closer. The simple choice $f(Z) = 2Z^2$ yields excellent results and will be assumed through out subsequent calculations. Thus in atomic units

$$\alpha_c = 2Z^2. \qquad\qquad (3.47)$$

Equation (3.45) gives two values of β for $\alpha_c = 2Z^2$. These values of β are substituted in equation (3.32) for calculating the energy eigen-values and the value of β for which the energy is minimum, is accepted. The equations (3.40) and (3.32) are used for calculating the ground state energy of six He-like atoms, i.e. from Z = 1 to Z = 6. The results are set out in Table I. The exact (experimental) results are given in a separate column. The values obtained for the pure coulomb potential, i.e. when $\alpha_c = \infty$ with and without the correlation factor are also shown. The relativistic corrections have not been included. It can be seen that one gets very good values with the modified potential. In each

case the improvement over the best H-F values (without the factor $g(r_{12})$) is of the order of 0.04 a.u. Thus the bulk of the correlation error is accounted for. The important point to note is that we get the near-exact value by using only one-variational-parameter along with the modified Coulomb potential. Such accuracies could be achieved with the usual Coulomb potential only on using a large number of variational parameters introduced in the wave function.[6] For example, Roothan[12] obtained an energy minimum for the ground state of He of the order of $E = 2.90036$ a.u., using the functions,

$$u(r) = e^{-\eta r} \sum_{n=0,2} a_n r^n , \qquad (3.48)$$

and the correlation factor

$$g(r_{12}) = 1 - e^{-\alpha r_{12}} \sum_{m=0,3} b_m r^m , \qquad (3.49)$$

which contained in all six variational parameters, namely α, η, a_0, a_2, b_0, b_3.

The energy value calculated with the modified Coulomb potential and only one variational parameter is much better than his results. However, it may be added that equation (3.40) with $m = 0$ gives

$$g(r_{12}) = 1 - e^{-\alpha r_{12}} b_0 ,$$

which is reminiscent of the factor occurring in the modified Coulomb potential taken here.

TABLE - I

Ground State Energies of He-like Systems

Z	β	E_{M-C} cf	$E_{C,H.F.}$	E_{C} cf	Improvement over E_C H.F.	Improvement over E_C cf	E exact (Experimental)
		a.u	a.u	a.u	a.u	a.u	a.u
1	0.5263	-0.5177	-0.4878	-0.4892	-0.0299	-0.0285	-0.5275
2	0.4758	-2.9032	-2.8617	-2.8760	-0.0415	-0.0272	-2.9037
3	0.4725	-7.2790	-7.2364	-7.2560	-0.0426	-0.0230	-7.2804
4	0.4275	-13.6520	-13.6113	-13.6340	-0.0407	-0.0180	-13.6572
5	0.4185	-22.0270	-21.9862	-22.0070	-0.0408	-0.0200	-22.0357
6	0.4095	-32.4011	-32.3612	-32.3830	-0.0399	-0.0181	-32.4171

$E_{M-C,cf}$ = Energy using the modified Coulomb potential with the correlation factor.

$E_{C,H-F}$ = Energy using the Coulomb potential and the Hartree-Fock method

$E_{C,cf}$ = Energy using the Coulomb potential with correlation factor.

The usual effective (average) Coulomb potential ϕ is the sum of the potential $\phi_p = \frac{Z}{r}$, due to ~~proton~~ nucleus and the potential ϕ_e, due to the electron, (the averaging is over the wave function

$$\Psi(r) = \frac{z^{3/2}}{\sqrt{\pi}} e^{-zr},$$

of the hydrogen atom in the ground state with

$$a = \hbar^2 = m = e = 1) \tag{3.50}$$

$$\phi(r) = \phi_p(r) + \phi_e(r) \tag{3.51}$$

$$= \frac{Z}{r} - \int \frac{\Psi(r')}{|r - r'|} d^3r' \tag{3.52}$$

The potential ϕ_e, is of course, the same as the potential of a static electron 'cloud' of density $\rho(r') = u^2(r')$. Hence the effective Coulomb potential is

$$\phi(r) = \frac{Z}{r} + (\frac{1}{r} + z) e^{-2r/a} \tag{3.53}$$

The effective (average) modified Coulomb potential $\phi(r)$ is derived as follows:

$$\phi(r) = \phi_p(r) + \phi_e(r)$$

$$= -\frac{Z}{r} + \int \frac{\Psi(r')}{|r-r'|}^2 (1 - e^{\alpha|r-r'|}) d^3r' \tag{3.54}$$

for $\frac{1}{|\underline{r}-\underline{r}'|}$ an expansion of Legendre functions is used and

$$\frac{1}{|\underline{r}-\underline{r}'|} = \frac{1}{r} \sum_{l=0} P_l(\cos\theta')(r'/r)^l \quad \text{if } r' < r \quad , \quad \Big\}$$

$$\qquad\qquad = \frac{1}{r'} \sum_{l=0} P_l(\cos\theta')(r/r')^l \quad \text{if } r' > r \quad \Big\} \qquad (3.55)$$

The wave function $\psi(\underline{r}')$ is

$$\psi(\underline{r}') = \frac{z^{3/2}}{\sqrt{\pi}} e^{-zr'} \quad \text{and,}$$

$$|\psi(\underline{r}')|^2 = \frac{z^3}{\pi} e^{-2zr'} \qquad (3.56)$$

Hence the effective modified Coulomb potential is

$$\emptyset(\underline{r}) = -\frac{z}{r} + \frac{z^3}{\pi} \int \frac{1}{|\underline{r}-\underline{r}'|} e^{-2zr'}(1-e^{-\alpha|\underline{r}-\underline{r}'|}d^3\underline{r}' \qquad (3.57)$$

$$= -\frac{z}{r} + \frac{z^3}{\pi} \int \frac{e^{-2zr'}}{|\underline{r}-\underline{r}'|} d^3\underline{r}' - \frac{e^2 z^3}{\pi} \int \frac{e^{-2zr'}e^{\alpha|\underline{r}-\underline{r}'|}}{|\underline{r}-\underline{r}'|} d^3\underline{r}'$$

$$\qquad\qquad\qquad\qquad \cdots\cdots\cdots (3.58)$$

If we split the integration over $\underline{r}'$ of the equation (3.58) into two parts ($\underline{r}' \ll r$ and $r' \gg r$), we see that in both parts integration over the angle θ' reduces the sums $\sum_{l=0}$ (of equation (3.44) to their first term ($l = 0$) by virtue of the orthogonality of the Legendre functions and we get the first integral of equation (3.58)

$$= \frac{Z^3}{\pi} \times 4\pi \left[\frac{1}{r} \int_0^r e^{-2Zr'} r'^2 dr' + \quad e^{-2Zr'} (r'^2/r') \, dr' \right], \quad \ldots\ldots(3.59)$$

(where integration over angular part gives 4π).

$$= 4Z^3 \left\{ \frac{1}{r} \left[e^{-2Zr'} \left(\frac{r'^2}{-2Z} - \frac{2r'}{4Z^2} - \frac{2}{8Z^3} \right) \right]_0^r \right.$$

$$\left. + \left[e^{-2Zr'} \left(\frac{r'^2}{-2Z} - \frac{1}{4Z^2} \right) \right]_r^\infty \right\} \quad (3.60)$$

$$= 4Z^3 \left\{ -\frac{1}{r} e^{-2Zr} \left(\frac{r^2}{2Z} + \frac{2r}{4Z^2} + \frac{2}{8Z^3} \right) + \frac{1}{r} \frac{2}{8Z^3} + \right.$$

$$\left. + e^{-2Zr} \left(\frac{r}{2Z} + \frac{1}{4Z^2} \right) \right\} \quad (3.61)$$

$$= \frac{1}{r} - e^{-2Zr} \left(Z + \frac{1}{r} \right) \quad (3.62)$$

The second integral in the equation (3.58) is

$$= \frac{Z^3}{\pi} \int \frac{e^{-2Zr'}}{r-r'} e^{-\alpha |r-r'|} d^3 r' \quad (3.63)$$

$$= \frac{Z^3}{\pi} 2 \times 2\pi \int \frac{e^{-2Zr'}}{|r-r'|} e^{-\alpha |r-r'|} r'^2 \, dr' \sin \theta' \, d\theta'$$

$$\ldots\ldots(3.64)$$

$$r'^2 \, dr' \sin \theta' d\theta' = |r-r'|^2 \, d|r-r'| \sin \theta_1 \, d\theta_1 \quad (3.65)$$

and

$$r'^2 = r^2 + |r-r'|^2 + 2r |r-r'| \cos \theta_1 \quad (3.66)$$

or

$$r' = \sqrt{r^2 + |r-r'|^2 \; 1 + 2r \, |r-r'| \cos \theta_1} \tag{3.67}$$

The integral (3.51) becomes

$$= z^3 \times 2 \int e^{-a \, |r-r'|} \; e^{-2Z \sqrt{r^2 + |r-r'|^2 + 2r \, |r-r'| \cos \theta_1}}$$

$$\times 2 \, |r-r'| \; d \, |r-r'| \; \sin \theta_1 \; d\theta_1 \tag{3.68}$$

$$= 2z^3 \int \frac{e^{-a \, |r-r'|} \, e^{-2Z \sqrt{x}}}{2r \, |r-r'|} \; d \, |r-r'| \; dx \, , \tag{3.69}$$

where

$$x = r^2 + |r-r'|^2 + 2 \, |r-r'| \cos \theta_1 \, ,$$

$$dx = - 2r \, |r-r'| \; \sin \theta_1 \; d\theta_1$$

The integral (3.69) becomes,

$$= \frac{z^3}{r} \; e^{-a \, |r-r'|} \; e^{-2Z \sqrt{x}} \; dx \; d|r-r'| \tag{3.70}$$

$$\int e^{-2Z \sqrt{x}} \; dx \quad = \quad \int e^{-2Zt} \; 2t \; dt$$

$$= - \frac{e^{-2Zt}}{Z} \, [\; t + \frac{1}{2Z} \,] \, , \tag{3.71}$$

where $\quad x = t^2, \quad dx = 2t dt$

From (3.70)

$$x = r^2 + |r - r'|^2 + 2r |r-r'| \cos \theta_1$$

Hence at

$$\theta_1 = \pi, \quad x = (r - |r-r'|)^2$$

and at

$$\theta_1 = 0, \quad x = (r + |r-r'|)^2$$

Hence from (3.69) we get

$$\int e^{-2Z\sqrt{x}} \, dx = \left[- \frac{e^{-2Zt}}{Z} (t + \frac{1}{2Z}) \right]_{(r+|r-r'|)}^{|r-|r-r'||}$$

$$= - e^{-2Z |r-|r-r'||} [|r-|r-r'|| + \frac{1}{2Z}]$$

$$+ \frac{e^{-2Z(r+|r-r'|)}}{Z} [r+|r-r'| + \frac{1}{2Z}] \qquad (3.72)$$

The second integral (3.69) becomes

$$= \frac{-Z^3}{rZ} \int e^{-\alpha |r-r'|} e^{-2Z |r-|r-r'||} [|r-|r-r'|| + \frac{1}{2Z}] \, d|r-r'|$$

$$+ \frac{Z^3}{rZ} \int e^{-\alpha |r-r'|} e^{-2Z(r+|r-r'|)} [r+|r-r'| + \frac{1}{2Z}] \, d|r-r'|,$$

$$\cdots\cdots (3.73)$$

where

$$I_1 = \frac{Z^3}{rZ} \int_0^r e^{-\alpha |r-r'|} e^{-2Z(r-|r-r'|)} [r-|r-r'| + \frac{1}{2Z}] \, d|r-r'|$$

$$- \frac{Z^3}{rZ} \int_\gamma^\infty e^{-\alpha |r-r'|} e^{-2Z(r-|r-r'|)} [|r-r'| -r + \frac{1}{2Z}] d|r-r'|$$

$$\cdots\cdots (3.74)$$

$$= \frac{Z^2}{r} \int_0^r e^{-2Zr} \, e^{-(\alpha-2Z)|r-r'|} \left(r + \frac{1}{2Z} - |r-r'| \right) d|r-r'|$$

$$- \frac{Z^2}{r} \int_r^\infty e^{2Zr} \, e^{-(\alpha+2Z)|r-r'|} \left(-r + \frac{1}{2Z} + |r-r'| \right) d|r-r'| \quad (3.75)$$

$$= \frac{Z^2}{r} e^{-2Zr} \left[\frac{(r+1/2Z) \, e^{-(\alpha-2Z)|r-r'|}}{-\alpha - 2Z} - \left(\frac{|r-r'|}{-(\alpha-2Z)} - \frac{1}{(\alpha-2Z)^2} \right) \right.$$

$$\left. e^{-(\alpha-2Z)|r-r'|} \right]_0^r$$

$$= \frac{Z^2}{r} e^{-2Zr} \left[\frac{(-r+1/2Z) \, e^{-(\alpha+2Z)|r-r'|}}{-(\alpha+2Z)} \left(\frac{|r-r'|}{(\alpha+2Z)} - \frac{1}{(\alpha+2Z)^2} \right) \right.$$

$$\left. e^{-(\alpha+2Z)|r-r'|} \right]_r^\infty \quad (3.76)$$

$$= \frac{Z^2}{r} \left[e^{-\alpha r} \left(\frac{-1}{2Z(\alpha-2Z)} + \frac{1}{(\alpha-2Z)^2} \right) \right]$$

$$- \frac{Z^2 e^{-2Zr}}{r} \left[\frac{r}{(\alpha-2Z)} + \frac{1}{2Z(\alpha-2Z)} - \frac{1}{(\alpha-2Z)^2} \right]$$

$$- \frac{Z^2 e^{-\alpha r}}{r} \left[\frac{1}{2Z(\alpha+2Z)} + \frac{1}{(\alpha+2Z)^2} \right], \quad (3.77)$$

and

$$I_2 = \frac{Z^2}{r} \int e^{-\alpha|r-r'|} \, e^{-2Z(r+|r-r'|)} \left(r + |r-r'| + \frac{1}{2Z} \right) d|r-r'|$$

$$\quad \cdots \cdots (3.78)$$

$$= \frac{Z^2}{r} \int \left[e^{-2Zr} e^{-(\alpha+2Z)|r-r'|} \left(r + \frac{1}{2Z} \right) + e^{-2Zr} e^{-(\alpha+2Z)|r-r'|} \times \right.$$

$$\left. \times |r-r'| \right] d|r-r'| \quad (3.79)$$

$$= \frac{Z^2 e^{-2Zr}}{r} \left[\left(r + \frac{1}{2Z} \right) \frac{e^{-(\alpha+2Z)|r-r'|}}{-(\alpha+2Z)} - \frac{e^{-(\alpha+2Z)|r-r'|}}{(\alpha+2Z)^2} \right]_0^\infty$$

$$\quad \cdots \cdots (3.80)$$

$$= \frac{Z^2 e^{-2Zr}}{r} \left[(r + \frac{1}{2Z}) \frac{1}{(\alpha + 2Z)} + \frac{1}{(\alpha + 2Z)^2} \right]. \qquad (3.81)$$

The second integral (3.61) becomes,

$$= I_1 + I_2$$

$$= \frac{Z^2}{r} e^{-\alpha r} \left[\frac{-1}{2Z(\alpha - 2Z)} + \frac{1}{(\alpha - 2Z)^2} \right]$$

$$- \frac{Z^2}{r} e^{-2Zr} \left[\frac{r}{(\alpha - 2Z)} + \frac{1}{2Z(\alpha - 2Z)} - \frac{1}{(\alpha - 2Z)^2} \right]$$

$$- \frac{Z^2}{r} e^{-\alpha r} \left[\frac{1}{2Z(\alpha + 2Z)} + \frac{1}{(\alpha + 2Z)} \right]$$

$$+ \frac{Z^2}{r} e^{-2Zr} \left[\frac{r}{(\alpha + 2Z)} + \frac{1}{2Z(\alpha + 2Z)} + \frac{1}{(\alpha + 2Z)^2} \right]. \qquad (3.82)$$

Hence the effective modified Coulomb potential from (3.62) and (3.79) is,

$$\phi(r) = - \frac{Z}{r} \frac{1}{r} - e^{-2Zr} (\frac{1}{r} + Z) - \frac{Z^2}{r} e^{-\alpha r} \left[\frac{-1}{2Z(\alpha - 2Z)} + \frac{1}{(\alpha - 2Z)^2} \right]$$

$$+ \frac{Z^2}{r} e^{-2Zr} \left[\frac{r}{(\alpha - 2Z)} + \frac{1}{2Z(\alpha - 2Z)} - \frac{1}{(\alpha - 2Z)^2} \right]$$

$$- \frac{Z^2}{r} e^{-\alpha r} \left[\frac{1}{2Z(\alpha + 2Z)} + \frac{1}{(\alpha + 2Z)^2} \right]$$

$$+ \frac{Z^2}{r} e^{-2Zr} \left[\frac{r}{(\alpha + 2Z)} + \frac{1}{2Z(\alpha + 2Z)} + \frac{1}{(\alpha + 2Z)^2} \right]. \qquad (3.83)$$

Hence for $\alpha \to \infty$ the modified Coulomb potential becomes the usual Coulomb potential given by (3.51)

2. APPLICATION TO THE EXCITED STATES

In this chapter we report the calculations for the excited 2S-2S state energy values using the modified Coulomb potential. For this we make use of the variational principle in its extended form. In general, if the wave functions $\Psi_1, \Psi_2, \ldots, \Psi_{n-1}, \Psi_n$ of the first n states arranged in order of increasing energy, are known, the wave function Ψ_{n+1} of the next energy-wise higher state gives a minimum of the integral $\langle \Psi | H | \Psi \rangle$ with the additional condition

$$\langle \Psi_{n+1} | H | \Psi_{n+1} \rangle = 1$$

and

$$\langle \Psi_{n+1} | \Psi_m \rangle = 0 \quad (m = 0, 1, \ldots n).$$

The successive orthogonalisation can be carried out following the Gram-Schmidt procedure.[26] The converse of the above is also true and can be made use of for determining Ψ_{n+1}. In this chapter we present a simple calculation for the state $|2s, 2s\rangle$ by making it orthogonal to the ground state $|1s, 1s\rangle$. Only in a more regorous calculation the state $|2s, 2s\rangle$ must be made orthogonal to the intermediate states e.g. $|1s, 2s\rangle$ as well.

The Hamiltonian used for this problem is given by the equation (3.3).

We choose a product function of one-electron hydrogen-like $2s$ orbitals with a correlation factor $g(r_{12})$, namely

$$\Psi(r_1, r_2, r_{12}) = u(r_1) \, u(r_2) \, g(r_{12}) \, / \, N^{1/2} \, , \qquad (3.84)$$

where

$$u(r) = \frac{z^{3/2}}{4\sqrt{2\pi}} \, (\, 2 - Zr) \, e^{-Zr/2} \qquad (3.85)$$

$$g(r_{12}) = (\, 1 + \beta' r_{12}) \qquad (3.86)$$

β' is a variational parameter. N is determined by the normalization constraint

$$\int \Psi \, \Psi^* d\tau = 1. \qquad (3.87)$$

We have

$$\int \Psi \Psi^* d\tau = \frac{z^6 \, 8\pi^2 \, \times \, 2}{N 32 \times 32\pi^2} \int_0^\infty e^{-Zr_1}(2 - Zr_1)^2 r_1 dr_1$$

$$\int_{r_1}^\infty e^{-Zr_2}(2 - Zr_2)^2 r_2 dr_2 \times \int_{r_2 - r_1}^{r_2 + r_1} (1 + \beta' r_{12})^2 r_{12} dr_{12}$$

$$= \frac{1}{N} \left[\, 1 + \frac{2167}{128} \, \frac{\beta'}{Z} + \frac{2763}{52} \, \frac{\beta'^2}{Z^2} \, \right]. \qquad (3.88)$$

From the equation (3.87) we get

$$\frac{1}{N} \left[\, 1 + \frac{2167}{128} \, \frac{\beta'}{Z} + \frac{2763}{52} \, \frac{\beta'}{Z^2} \, \right] = 1. \qquad (3.89)$$

Hence,

$$N = 1 + \frac{2167}{128} \frac{\beta'}{Z} + \frac{2763}{32} \frac{\beta'^2}{Z^2} . \qquad (3.90)$$

Now

$$(\nabla_1^2 + \nabla_2^2)\Psi = \frac{\partial^2 \Psi}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial \Psi}{\partial r_1} + \frac{\partial^2 \Psi}{\partial r_2^2} + \frac{2}{r_2} \frac{\partial \Psi}{\partial r_2}$$

$$+ \frac{2 \partial^2 \Psi}{\partial r_{12}^2} + \frac{4}{r_{12}} \frac{\partial \Psi}{\partial r_{12}}$$

$$+ \frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} + \frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \frac{\partial^2 \Psi}{\partial r_2 \partial r_{12}} .$$

$$\cdots\cdots (3.91)$$

Further

$$\frac{\partial \Psi}{\partial r_1} = \frac{Z^3}{32\sqrt{N}} [-2Z + \frac{Z^2}{2} - r_1](2 - Zr_2)e^{-Zr_1/2} e^{-Zr_2/2} (1 + \beta' r_{12}),$$

$$\cdots\cdots (3.92)$$

$$\frac{\partial \Psi}{\partial r_2} = \frac{Z^3}{32\sqrt{N}} [-2Z + \frac{Z^2}{2} r_2](2 - Zr_1)e^{-Zr_1/2} e^{-Zr_2/2} (1 + \beta' r_{12}),$$

$$\cdots\cdots (3.93)$$

$$\frac{\partial^2 \Psi}{\partial r_1^2} = \frac{Z^3}{32\sqrt{N}} [\frac{3}{2} Z^2 - \frac{Z^3}{4} r_1](2 - Zr_2)e^{-Zr_1/2} d^{-Zr_2/2} (1 + \beta' r_{12})$$

$$(3.94)$$

$$\frac{\partial^2 \Psi}{\partial r_2^2} = \frac{Z^3}{32\sqrt{N}} [\frac{3}{2} Z^2 - \frac{Z^3}{4} r_2](2 - Zr_1)e^{-Zr_1/2} e^{-Zr_2/2} (1 + \beta' r_{12})$$

$$(3.95)$$

$$\frac{\partial \Psi}{\partial r_{12}} = \frac{Z^3}{32\pi\sqrt{N}} \beta'(2-Zr_1)(2-Zr_2) e^{-Zr_1/2} e^{-Zr_2/2}, \qquad (3.96)$$

$$\frac{\partial^2 \Psi}{\partial r_{12}^2} = 0 ,$$

$$\frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} = \frac{Z^3 \beta'}{32\pi\sqrt{N}} (-2Z + \frac{Z^2}{2} r_1)(2-Zr_2) e^{-Zr_1/2} e^{-Zr_2/2}, \qquad (3.97)$$

and

$$\frac{\partial^2 \Psi}{\partial r_2 \partial r_{12}} = \frac{Z^3 \beta'}{32\pi\sqrt{N}} (-2Z + \frac{Z^2}{2} r_2)(2-Zr_1) e^{-Zr_1/2} e^{-Zr_2/2} . \qquad (3.98)$$

Hence from the equation (3.91)

$$(\nabla_1^2 + \nabla_2^2)\Psi = \frac{Z^3}{32\pi\sqrt{N}} [(\frac{3}{2}Z^2 - \frac{Z^3}{4} r_1)(2-Zr_2)(1+\beta' r_{12})$$

$$+ \frac{2}{r_1} (-2Z + \frac{Z^2}{2} r_1)(2-Zr_2)(1+\beta' r_{12})$$

$$+ (\frac{3}{2}Z^2 - \frac{Z^3}{4} r_2)(2-Zr_1)(1+\beta' r_{12})$$

$$+ \frac{2}{r_{12}} (-2Z + \frac{Z^2}{2} r_2)(2-Zr_1)(1+\beta' r_{12})$$

$$+ \frac{4}{r_{12}} \beta'(2-Zr_1)(2-Zr_2)$$

$$+ \frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}} \beta'(-2Z + \frac{Z^2}{2} r_1)(2-Zr_2)$$

$$+ \frac{r_{12}^2 + r_2^2 - r_1^2}{r_2 r_{12}} \beta'(-2Z + \frac{Z^2}{2} r_2)(2-Zr_1)]$$

$$\times e^{-Zr_1} e^{-Zr_2} . \qquad (3.99)$$

$$\frac{-1}{2}(\nabla_1^2 + \nabla_2^2)\psi = \frac{z^3}{32\pi\sqrt{N}}\left[\left\{\left(-\frac{3}{2x^2}z^2 + \frac{z^3}{8}r_1\right)(2-zr_2)\right.\right.$$

$$+ \left(\frac{2z}{r_1} - \frac{z^2}{2}\right)(2-zr_2) + \left(\frac{-3}{4}z^2 + \frac{z^3}{8}r_2\right)(2-zr_1)$$

$$+ \left(\frac{2z}{r_2} - \frac{z^2}{2}\right)(2-zr_1)\right\} \times (1+\beta'r_{12})$$

$$+ \left\{\frac{-2}{r_{12}}(2-zr_1)(2-zr_2)\right.$$

$$+ \frac{r_{12}^2 + r_1^2 - r_2^2}{r_1 r_{12}}\left(z - \frac{z^2}{4}r_1\right)(2-zr_2)$$

$$+ \left.\left.\frac{r_{12}^2 + r_2^2 - r_1^2}{r_1 r_{12}}\left(z - \frac{z^2}{4}r_2\right)(2-zr_1)\right\} \times \beta'\right]$$

$$\times e^{-zr_1} e^{-zr_2} \qquad . \tag{3.100}$$

Next consider the term,

$$-z\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi$$

$$= -\frac{z^3}{32\pi\sqrt{N}}\left[\left(\frac{2z}{r_1} - z^2\right)(2-zr_2) + \left(\frac{2z}{r_2} - z^2\right)(2-zr_1)\right] \times$$

$$\times (1 + \beta'r_{12})\, e^{-zr_1/2}\, e^{-zr_2/2} \tag{3.101}$$

$$= -\frac{z^3}{32\pi\sqrt{N}}\left[\left(-\frac{2z}{r_1} + z^2\right)(2-zr_2) + \left(\frac{-2z}{r_2} + z^2\right)(2-zr_1)\right]$$

$$\times (1 + \beta'r_{12})\, e^{-zr_1/2}\, e^{-zr_2/2} \quad . \tag{3.102}$$

Adding the equations (3.100) and (3.101), we get

$$- \frac{1}{2} (\nabla_1^2 + \nabla_2^2) \Psi - Z(\frac{1}{r_1} + \frac{1}{r_2}) \Psi$$

$$= \frac{Z^3}{32\pi \sqrt{N}} [\{ (\frac{-3}{4}Z^2 + \frac{Z^3}{8}r_1)(2-Zr_2) + \frac{Z^2}{2} (2-Zr_2)$$

$$+ \frac{Z^2}{2}(2-Zr_1) + (\frac{-3}{4}Z^2 + \frac{Z^3}{8} r_2)(2-Zr_1) \} (1+\beta'r_{12})$$

$$+ \{ \frac{-2}{r_{12}} (2-Zr_1)(2-Zr_2) + \frac{r_{12}^2+r_1^2-r_2^2}{r_1 r_{12}} (Z - \frac{Z^2}{4}r_1)(2-Zr_2)$$

$$+ \frac{r_{12}^2+r_2^2-r_1^2}{r_2 r_{12}} (Z - \frac{Z^2}{4}r_2)(2-Zr_1) \} \times \beta'] \times e^{-Zr_1/2} e^{-Zr_2/2}$$

$$(3.103)$$

Hence from the equation (3.3) the Hamiltonian is given by

$$H\Psi = - \frac{Z^3}{32\pi \sqrt{N}} [(-Z^2 + \frac{Z^3}{2}(r_1+r_2) - \frac{Z^4}{4}r_1 r_2)(1+\beta'r_{12})$$

$$+ \beta' \{ \frac{r_{12}}{r_1 r_2} [2Z(r_1+r_2) - Z^2(r_1^2+r_2^2) - Z^2 r_1 r_2 + \frac{Z^3}{4}r_1 r_2 (r_1+r_2)]$$

$$+ \frac{r_1^2 - r_2^2}{r_1 r_2 r_{12}} [2Z(r_2-r_1) + Z^2(r_1^2-r_2^2) + \frac{Z^3}{4}r_1 r_2 (r_2-r_1)]$$

$$- \frac{2}{r_{12}} (2 - Zr_1) (2 - Zr_2) \}$$

$$+ \frac{1}{r_{12}} (1 - e^{-\alpha} e^{r_{12}})(2-Zr_1)(2-Zr_2) \times (1+\beta'r_{12})] \times e^{-Zr_1/2} e^{-Zr_2/2} .$$

$$(3.104)$$

The energy expectation value

$$E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$$

is calculated by using the expression for $H\Psi$ from the
equation (3.104), we have

$$E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$$

$$= I_1 + I_2 + I_3 + I_4 + I_5 + I_6 + I_7 + I_8 + I_9 + I_{10} + I_{11} + I_{12} , \tag{3.105}$$

where

$$I_1 = \frac{-z^6 16\pi^2 z^2}{N 32 \times 32 \pi^2} \int_0^\infty e^{-zr_1} r_1 (2-zr_1) dr_1 \int_{r_1}^\infty e^{-zr_2} r_2 (2-zr_2) dr_2 \; \times$$

$$\times \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12})^2 r_{12} dr_{12}$$

$$= \frac{1}{N} \left[-\frac{z^2}{16} - \frac{63 z\beta'}{64} - \frac{9\beta'^2}{2} \right], \tag{3.106}$$

$$I_2 = \frac{z^6 8 \times 2\pi^2}{N 32 \times 32\pi^2} \frac{z^3}{2} \int_0^\infty e^{-zr_1} r_1 (2-zr_1) dr_1 \; \times$$

$$\times \int_{r_1}^\infty e^{-zr_2} r_2 (r_1+r_2)(2-zr_2) dr_2 \; \times \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12})^2 dr_{12}$$

$$= \frac{1}{N} \left(\frac{3}{8} z^2 + \frac{777}{128} z\beta' + \frac{57}{2} \beta'^2 \right), \tag{3.107}$$

$$I_3 = \frac{-z^{10} 8 \times 2\pi^2}{N 32 \times 32\pi^2} \frac{1}{4} \int_0^\infty e^{-zr_1} r_1^2 (2-zr_1) dr_1 \; \times$$

$$\times \int_{r_1}^\infty e^{-zr_2} (2-zr_2) r_2^2 dr_2 \; \times \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12})^2 r_{12} dr_{12}$$

$$= \frac{-1}{N} \left[\frac{9}{8} z^2 + \frac{4771}{16 \times 32} z\beta' + \frac{21465}{16 \times 32} \beta'^2 \right], \tag{3.108}$$

$$I_4 = \frac{Z^6 16\pi^2 2Z\beta'}{N32 \times 32\pi^2} \int_0^\infty e^{-Zr_1} r_1(2-Zr_1) dr_1 \times$$

$$\times \int_{r_1}^\infty \frac{e^{-Zr_2} r_2(r_1+r_2)(2-Zr_2) dr_2}{r_1 r_2} \times \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12}) r_{12}^2 dr_{12}$$

$$= \frac{1}{N}\left[-\frac{5}{8} Z\beta' + \frac{3}{2}\beta'^2 \right], \qquad (3.109)$$

$$I_5 = \frac{-Z^8 16 \times \beta' \pi^2}{N32 \times 32\pi^2} \int_0^\infty e^{-Zr_1} r_1(2-Zr_1) dr_1 \times$$

$$\times \int_{r_1}^\infty \frac{e^{-Zr_2}(r_1^2+r_2^2)(2-Zr_2) r_2 dr_2}{r_1 r_2} \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12}) r_{12}^2 dr_{12}$$

$$= \frac{-1}{N}\left[\frac{17}{64} Z\beta' + \frac{9}{2}\beta'^2 \right], \qquad (3.110)$$

$$I_6 = \frac{-Z^8 \times 16\pi^2 \times \beta'}{N32 \times 32\pi^2} \int_0^\infty e^{-Zr_1} r_1(2-Zr_1) dr_1 \times$$

$$\times \int_{r_1}^\infty \frac{e^{-Zr_2} r_2(2-Zr_2) r_1 r_2 dr_2}{r_1 r_2} \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12}) r_{12}^2 r_{12}$$

$$= \frac{-1}{N}\left[\frac{63}{128} Z\beta' + \frac{9}{2}\beta'^2 \right], \qquad (3.111)$$

$$I_7 = \frac{Z^6 \times Z^3 \times 16\pi^2 \beta'}{N \times 32 \times 32\pi^2 \times 4} \int_0^\infty e^{-Zr_1} r_1(2-Zr_1)dr_1 \quad \times$$

$$\times \int_{r_1}^\infty \frac{e^{-Zr_2} r_2(2-Zr_2) r_1 r_2(r_1+r_2)dr_2}{r_1 r_2} \int_{r_2-r_1}^{r_2+r_1} (1+\beta'r_{12})r_{12}^2 dr_{12}$$

$$= \frac{1}{N}\left[\frac{777}{512} Z\beta' + \frac{57}{4}\beta'^2 \right], \tag{3.112}$$

$$I_8 = \frac{Z^6 \times 16\pi^2 \times 2Z\beta'}{N \times 32 \times 32\pi^2} \int_0^\infty e^{-Zr_1} r_1(2-Zr_1)dr_1 \quad \times$$

$$\times \int_{r_1}^\infty \frac{e^{-Zr_2}(r_1^2-r_2^2)(r_2-r_1)r_2 dr_2}{r_1 r_2} \int_{r_2-r_1}^{r_2+r_1} \frac{(1+\beta'r_{12})r_{12}dr_{12}}{r_{12}}$$

$$= \frac{1}{N}\left[\frac{17}{64} Z\beta' + \frac{3}{2}\beta'^2 \right], \tag{3.113}$$

$$I_9 = \frac{-Z^6 \times Z^2 \times 16\pi^2 \beta'}{N 32 \times 32\pi^2} \int_0^\infty e^{-Zr_1} r_1(2-Zr_1)dr_1 \quad \times$$

$$\times \int_{r_1}^\infty \frac{e^{-Zr_2}(r_1^2-r_2^2)(r_1^2-r_2^2)dr_2}{r_1 r_2} \int_{r_2-r_1}^{r_2+r_1} \frac{(1+\beta'r_{12})r_{12}dr_{12}}{r_{12}}$$

$$= \frac{-1}{N}\left[\frac{3}{4} Z\beta' + \frac{9}{2}\beta'^2 \right], \tag{3.114}$$

$$I_{10} = \frac{z^6 \times z^3 \times 16\pi^2 \beta'}{N \times 32 \times 32\pi^2 \times 4} \int_0^\infty e^{-Zr_1} r_1 (2-Zr_1) dr_1 \times$$

$$\times \int_{r_1}^\infty \frac{e^{-Zr_2}(2-Zr_2) r_2 (r_1^2 - r_2^2)(r_2 - r_1) r_1 r_2 dr_2}{r_1 r_2} \times$$

$$\times \int_{r_2-r_1}^{r_2+r_1} \frac{(1+\beta' r_{12}) r_{12} dr_{12}}{r_{12}}$$

$$= \frac{1}{N} \left[\frac{27}{16 \times 32} Z\beta' + \frac{3}{4} \beta'^2 \right], \tag{3.115}$$

$$I_{11} = \frac{-z^6 \times 16\pi^2 \times 2\beta'}{N 32 \times 32\pi^2} \int_0^\infty e^{-Zr_1} r_1 (2-Zr_1)^2 dr_1 \times$$

$$\times \int_{r_1}^\infty e^{-Zr_2} r_2 (2-Zr_2)^2 dr_2 \int_{r_2-r_1}^{r_2+r_1} \frac{(1+\beta' r_{12}) r_{12} dr_{12}}{r_{12}}$$

$$= \frac{-1}{N} \left[\frac{77}{256} Z\beta' + 2\beta'^2 \right], \tag{3.116}$$

$$I_{12} = \frac{z^6 \times 16\pi^2}{N 32 \times 32\pi^2} \int_0^\infty e^{-Zr_1} r_1 (2-Zr_1)^2 dr_1 \int_{r_2}^\infty e^{-Zr_2} r_1 (2-Zr_2)^2 dr_2 \times$$

$$\times \int_{r_2-r_1}^{r_2+r_1} \frac{(1+\beta' r_{12})^2 r_{12}(1-e^{-\alpha_c r_{12}}) dr_{12}}{r_{12}}$$

$$= I_{12.1} + I_{12.2}, \tag{3.117}$$

where

$$I_{12.1} = \frac{Z^6}{N64} \int_0^\infty e^{-Zr_1} r_1 (2-Zr_1)^2 dr_1 \int_{r_1}^\infty e^{-Zr_2} r_2 (2-Zr_2)^2 dr_2 \times$$

$$\times \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12})^2 dr_{12}$$

$$= \frac{1}{N} \left[\frac{77Z}{32 \times 16} + 2\beta' + \frac{2167}{32 \times 8} \beta'^2 \frac{1}{Z} \right], \qquad (3.118)$$

and

$$I_{12.2} = \frac{Z^6}{N64} \int_0^\infty e^{-Zr_1} r_1 (2-Zr_1)^2 dr_1 \int_{r_1}^\infty e^{-Zr_2} r_2 (2-Zr_2)^2 dr_2 \times$$

$$\times \int_{r_2-r_1}^{r_2+r_1} (1+\beta' r_{12})^2 e^{-\alpha_c r_{12}} dr_{12} . \qquad (3.119)$$

The integral

$$\int_{r_2-r_1}^{r_2+r_2} (1+\beta' r_{12})^2 e^{-\alpha_c r_{12}} dr_{12} =$$

$$= - e^{-\alpha_c r_2} \left\{ (e^{-\alpha_c r_1} - e^{\alpha_c r_1}) \left[\frac{1}{\alpha_c} + \frac{2\beta'}{\alpha_c^2} + \frac{2\beta'^2}{\alpha_c^3} \right] \right.$$

$$+ (e^{-\alpha_c r_1} - e^{+\alpha_c r_1}) \left[\frac{2\beta'}{\alpha_c} + \frac{2\beta'^2}{\alpha_c^2} \right] r_2$$

$$+ (e^{-\alpha_c r_1} + e^{\alpha_c r_1}) \left[\frac{2\beta'}{\alpha_c} \frac{2\beta'^2}{\alpha_c^2} \right] r_1$$

$$+ (e^{-\alpha_c r_1} - e^{\alpha_c r_1}) (r_1^2 + r_2^2) \left(\frac{\beta'^2}{\alpha_c} \right)$$

$$+ \left. (e^{-\alpha_c r_1} + e^{\alpha_c r_1}) \left[\frac{2\beta'^2}{\alpha_c} r_1 r_2 \right] \right\} \qquad (3.120)$$

Hence the integral

$$L_{12.2} = I_a + I_b + I_c + I_d + I_e , \qquad (3.121)$$

where

$$I_a = \frac{Z^6}{N64} [\frac{1}{a_c} + \frac{2a'}{a_c^2} + \frac{2a'^2}{a_c^3}] \int_0^\infty e^{-Zr_1}(e^{-a_c r_1} - e^{a_c r_1}) \times$$

$$\times\, r_1(2-Zr_1)^2 dr_1 \int_{r_1}^\infty e^{-(Z+a_c)r_2} r_2(2-Zr_2)^2 dr_2$$

$$= \frac{\frac{1}{a_c} + \frac{2a'}{a_c^2} + \frac{2a'^2}{a_c^3}}{64N} [\frac{18Z^4}{(Z+a_c)^8} - \frac{48Z^3}{(Z+a_c)^7} + \frac{56Z^2}{(Z+a_c)^6} - \frac{32Z}{(Z+a_c)^5} +$$

$$+ \frac{23}{4(Z+a_c)^4} - \frac{5}{8} \times \frac{1}{Z^3(Z+a_c)} - \frac{5}{8} \times \frac{1}{Z^2(Z+a_c)^2} - \frac{3}{2} \times \frac{1}{Z(Z+a_c)^3}],$$

$$\qquad (3.122)$$

$$I_b = \frac{Z^6}{N64} [\frac{2a'}{a_c} + \frac{2a'^2}{a_c^2}] \int_0^\infty e^{-Zr_1}(e^{-a_c r_1} - e^{a_c r_1}) \times$$

$$\times\, r_1(2-Zr_1)^2 dr_1 \int_{r_1}^\infty e^{-(Z+a_c)r_2} r_2^2(2-Zr_2)^2 dr_2$$

$$= \frac{Z^6}{N64} [\frac{1467}{16} \frac{Z^4}{(Z+a_c)^9} - \frac{441}{2} \frac{Z^3}{(Z+a_c)^8} + \frac{228Z^2}{(Z+a_c)^7} - \frac{110Z}{(Z+a_c)^6} -$$

$$- \frac{2}{(Z^3(Z+a_c)^2)} - \frac{27}{16Z^4(Z+a_c)} + \frac{13}{(Z+a_c)^5} - \frac{3}{2} \frac{1}{Z^2(Z+a_c)^3}$$

$$+ \frac{3}{Z(Z+a_c)^4}], \qquad (3.123)$$

$$c = \frac{Z^6}{N64} \left[\frac{2\beta'}{\alpha_c} + \frac{2\beta'^2}{\alpha_c^2} \right] \int_0^\infty e^{-Zr_1}(e^{-\alpha_c r_1} + e^{\alpha_c r_1}) \times$$

$$\times \, r_1^2(2-Zr_1)^2 dr_1 \times \int_{r_1}^\infty e^{-(Z+\alpha_c)r_2} r_2(2-Zr_2)^2 dr_2$$

$$= \frac{Z^6}{N64} \left[\frac{2\beta'}{\alpha_c} + \frac{2\beta'^2}{\alpha_c^2} \right] \left[\frac{857}{16} \frac{Z^4}{(Z+\alpha_c)^9} - \frac{231}{2} \frac{Z^3}{(Z+\alpha_c)^8} \right.$$

$$+ \frac{108Z^2}{(Z+\alpha_c)^7} - \frac{50Z}{(Z+\alpha_c)^6} + \frac{10}{(Z+\alpha_c)^5} + \frac{27}{16} \frac{1}{Z^4(Z+\alpha_c)}$$

$$\left. + \frac{11}{8} \times \frac{1}{Z^3(Z+\alpha_c)^2} + \frac{1}{4Z^2} \frac{1}{(Z+\alpha_c)^3} + \frac{3}{2Z(Z+\alpha_c)^3} \right], \quad (3.124)$$

$$I_d = \frac{Z^6}{N64} \frac{\beta'^2}{\alpha_c} \int_0^\infty e^{-Zr_1}(e^{-\alpha_c r_1} - e^{\alpha_c r_1}) r_1(2-Zr_1)^2 dr_1 \times$$

$$\times \int_{r_1}^\infty e^{-(Z+\alpha_c)r_2}(r_1^2+r_2^2) r_2(2-Zr_2)^2 dr_2$$

$$= \frac{\beta'^2 Z^6}{N\alpha_c 64} \left[\frac{720Z^4}{(Z+\alpha_c)^{10}} - \frac{1536Z^3}{(Z+\alpha_c)^9} + \frac{1392Z^2}{(Z+\alpha_c)^8} - \frac{576Z}{(Z+\alpha_c)^7} + \right.$$

$$+ \frac{51}{(Z+\alpha_c)^6} - \frac{33}{2} \frac{1}{Z^5(Z+\alpha_c)} - \frac{33}{2Z^4(Z+\alpha_c)^2}$$

$$\left. - \frac{57}{4} Z^3 \frac{1}{(Z+\alpha_c)^3} - \frac{39}{4Z^2} \frac{1}{(Z+\alpha_c)^4} + \frac{6}{Z(Z+\alpha_c)^5} \right], \quad (3.125)$$

$$I_e = \frac{Z^6}{N64} \times \frac{2\beta'^2}{\alpha_c} \int\limits_0^\infty e^{-Zr_1}(e^{-\alpha_c r_1} + e^{\alpha_c r_1}) r_1^2 (2-Zr_1)^2 dr_1 \times$$

$$\times \int\limits_{r_1}^\infty e^{-(Z+\alpha_c)r_2} r_2^2 (2-Zr_2)^2 dr_2$$

$$= \frac{Z^6}{N64} \frac{2\beta'^2}{\alpha_c} \left[\frac{288Z^4}{(Z+\alpha_c)^{10}} - \frac{576Z^3}{(Z+\alpha_c)^9} + \frac{480Z^2}{(Z+\alpha_c)^8} - \frac{192Z}{(Z+\alpha_c)^7} \right.$$

$$+ \frac{32}{(Z+\alpha_c)^6} + \frac{33}{4} \frac{1}{Z^5(Z+\alpha_c)} + \frac{33}{4} \frac{1}{Z^4(Z+\alpha_c)^2}$$

$$\left. + \frac{13}{2} \frac{1}{Z^3(Z+\alpha_c)^3} + \frac{3}{Z^2(Z+\alpha_c)^4} + \frac{6}{Z(Z+\alpha_c)^5} \right].$$

$$(3.126)$$

The total integral I_{12} is the sum of the integrals given by the equations (3.122) to (3.126).

Adding all the integrations we get the expression for the energy

$$E = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$$

$$= \frac{1}{N} \left[-\frac{1}{4}Z^2 + \frac{77Z}{512} - \frac{2527Z\beta'}{512} + 2\beta' - \frac{8665\beta'}{512} + \frac{2167}{256}\frac{\beta'^2}{Z} \right],$$

$$+ \frac{Z^6}{N64} \oint \left(\frac{1}{\alpha_c} + \frac{2\beta'}{\alpha_c^2} + \frac{2\beta'^2}{\alpha_c^3} \right) \times \left[\frac{18Z^4}{(Z+\alpha_c)^8} - \frac{48Z^3}{(Z+\alpha_c)^7} + \right.$$

$$+ \frac{56Z^2}{(Z+\alpha_c)^6} - \frac{32Z}{(Z+\alpha_c)^5} + \frac{23}{4}\frac{1}{(Z+\alpha_c)^4} - \frac{5}{8Z^3(Z+\alpha_c)} -$$

$$- \frac{5}{(8Z^2(Z+\alpha_c)^2} - \frac{3}{2}\frac{1}{Z(Z+\alpha_c)^3} \left. \right]$$

$$+ \left(\frac{2\beta'}{\alpha_c} + \frac{2\beta'^2}{\alpha_c^2} \right) \left[\frac{1467}{16}\frac{Z^4}{(Z+\alpha_c)^9} - \frac{4412Z^3}{2(Z+\alpha_c)^8} + \right.$$

$$+ \frac{228Z^2}{(Z+\alpha_c)^7} - \frac{110Z}{(Z+\alpha_c)^6} + \frac{13}{(Z+\alpha_c)^5} - \frac{27}{16Z^4(Z+\alpha_c)} -$$

$$- \frac{3}{2}\frac{1}{Z^2(Z+\alpha_c)^3} + \frac{3}{Z(Z+\alpha_c)^4} - \frac{2}{Z^3(Z+\alpha_c)^2} \left. \right]$$

$$+ \left(\frac{2\beta'}{\alpha_c} + \frac{2\beta'^2}{\alpha_c^2} \right) \left[\frac{837}{16}\frac{Z^4}{Z(Z+\alpha_c)^9} - \frac{231Z^3}{2(Z+\alpha_c)^8} + \frac{108Z^2}{(Z+\alpha_c)^7} \right.$$

$$- \frac{50Z}{(Z+\alpha_c)^6} + \frac{10}{(Z+\alpha_c)^5} + \frac{27}{16}\frac{1}{Z^4(Z+\alpha_c)} + \frac{11}{8Z^3(Z+\alpha_c)^2}$$

$$+ \frac{1}{4Z^3(Z+\alpha_c)^3} + \frac{3}{2Z(Z+\alpha_c)^4} \left. \right]$$

$$+ \frac{\beta'^2}{a_c} \left[\frac{720z^4}{(z+a_c)}10 - \frac{1536z^3}{(z+a_9)}9 + \frac{1392z^2}{(z+a_9)}8 - \frac{576z}{(z+a_c)}7 + \frac{51}{(z+\alpha_c)}6 \right.$$

$$- \frac{57}{4} \frac{1}{z^3(z+\alpha_c)^3} - \frac{33}{2z^5(z+a_c)} - \frac{33}{2z^4(z+a_c)^2} - \frac{39}{4} \frac{1}{z^2(z+\alpha_c)^4} + \frac{6}{z(z+\alpha_c)}$$

$$- \frac{2\beta'^2}{a_c} \left[\frac{288z^4}{(z+a_c)}10 - \frac{576z^3}{(z+a_c)}9 + \frac{480z^2}{(z+a_c)}8 - \frac{192z}{(z+a_c)}7 \right.$$

$$+ \frac{32}{(z+a_c)}6 + \frac{33}{4z^5(z+a_c)} + \frac{33}{4} \frac{1}{z^4(z+a_c)^2}$$

$$\left. + \frac{15}{2z^3(z+a_c)^3} + \frac{3}{z^2(z+a_c)^4} + \frac{6}{z(z+a_c)^5} \right] \Bigg\} . \tag{3.127}$$

The parameter β' is calculated by orthogonalizing the wave function for the $2S$ orbitals to the ground state wave function, i.e.

$$\int \Psi_{2S} \Psi_{1S} \, d\tau = 0, \tag{3.128}$$

where

$$\int \Psi_{2S} \Psi_{1S} \, d\tau = \int_0^\infty e^{-\frac{3}{2}zr_1}(2-zr_1)r_1 dr_1 \quad x$$

$$x \int_{r_1}^\infty e^{-(3/2)zr_2}(2-zr_2)r_2 dr_2 \quad x$$

$$x \int_{r_2-r_1}^{r_2+r_1} (1+\beta r_{12})(1+\beta' r_{12})r_{12} dr_{12}$$

$$= - \frac{896}{39} (\beta + \beta') \tag{3.129}$$

Hence the orthogonality condition is

$$\beta' = -\beta \quad .$$

This gives the value of β' in terms of β. The values of β for different values of Z are given in the table 1. Hence, for each value of Z we get a value of β'.

It may be noted that the negative sign of β' will have the effect of making the correlated trial wave function (c.f.(3.86)) non-nodeless. This however, is theoretically possible as the wave function in question does not represent the ground state.

The excited state (2s - 2s) energies can now be evaluated by substituting the values of β' into the energy expression (3.127). A trial calculation made for the case of helium, however, yielded energy value far in excess of the correct value, irrespective of the value of a_c chosen. This indicates the inadequacy of the present procedure, namely, making the one-parameter trial function orthogonal to the ground state for the case of excited states. It is of some interest to note that the excited state energy values obtained by independent variation of β' in the correlated wave functions are far better than those obtained through the ortho-gonalisation procedure. Proceeding exactly as in section 1, the energy function turns out to be

$$E = \frac{1}{N} [A_1 + B_1\beta' + C_1\beta'^{2c}]^2 ,$$

where,

$$A_1 = -\frac{z^2}{4} + \frac{77}{512} z + \frac{z^6}{64} \frac{1}{a_c} D_I .$$

$$B_1 = -\frac{2527}{512} z + 2 + \frac{2z^6}{64} (-\frac{1}{a_c^2} D_I + \frac{1}{a_c} D_{II})$$

$$C_1 = -\frac{8665}{512} + \frac{2167}{256} \frac{1}{z} + \frac{z^6}{64} (-\frac{2}{a_c^3} D_I + \frac{2}{a_c^2} D_{II} + \frac{1}{a_c} D_{III})$$

with

$$D_I = \frac{18z^4}{(z+a_c)^8} - \frac{48z^3}{(z+a_c)^7} + \frac{56z^2}{(z+a_c)^6} - \frac{32z}{(z+a_c)^5} + \frac{23}{4} \frac{1}{(z+a_c)^4}$$
$$- \frac{5}{8z^3(z+a_c)} - \frac{5}{8z^2(z+a_c)^2} - \frac{3}{2} \frac{1}{z(z+a_c)^3} ,$$

$$D_{II} = \frac{144z^4}{(z+a_c)^9} - \frac{336z^3}{(z+a_c)^8} + \frac{336z^2}{(z+a_c)^7} - \frac{160z}{(z+a_c)^6} + \frac{23}{(z+a_c)^5}$$
$$- \frac{5}{4z^2(z+a_c)^3} - \frac{9}{2z(z+a_c)^4} - \frac{5}{2z^3(z+a_c)^2} ,$$

$$D_{III} = \frac{1296z^4}{(z+a_c)^{10}} - \frac{2788z^3}{(z+a_c)^9} + \frac{2352z^2}{(z+a_c)^8} - \frac{960z}{(z+a_c)^7} +$$
$$+ \frac{115}{(z+a_c)^6} - \frac{5}{4z^3(z+a_c)^3} - \frac{27}{4z^2(z+a_c)^4} + \frac{18}{z(z+a_c)^5} .$$

β' is given by $\frac{\partial E}{\partial \beta'} = 0 ,$ or

$$\left[B_1 - \frac{2167}{128} \frac{A_1}{Z} \right] + \left[2C_1 - \frac{2763}{16} \frac{A_1}{Z^2} \right] \beta +$$

$$+ \left[\frac{2167}{128} \frac{C_1}{Z} - \frac{2763}{32} \frac{B_1}{Z^2} \right] \beta'^2 \qquad = \qquad 0.$$

Choosing $\alpha_c = 2Z^2$ as in section 1 the values of α' for the different systems are

$$\beta'_{He} = 0.1414, \quad - 0.2194$$

$$\beta'_{Li^+} = 0.0453, \quad - 0.34635$$

$$\beta'_{Be^{++}} = 0.2329, \quad - 0.4427$$

The corresponding lowest energy values are

$$E_{He}(2s-2s) = -0.856438 - 0.0005306 = -0.856968 \text{ a.u.}$$

$$E_{Li^+}(2s-2s) = -1.888061 - 0.0006149 = -1.888675 \text{ a.u.}$$

$$E_{Be^{++}}(2s-2s) = -3.657815 - 0.000271 = -3.658086 \text{ a.u.}$$

(The second quantity in the middle of column gives the contribution of α_c).

These are far better than those values obtained by orthogonalisation, some of which were even positive. In any case, the correlation effect and, therefore, the role of α_c is less dominant for excited states as the electrons are on the average further apart.

C H A P T E R - 4

APPLICATION TO HYDROGEN-LIKE ONE-ELECTRON ATOMS

(Lamb-Shift)

As is well-known, the pure Coulomb potential leads to accidental degeneracy for one-electron hydrogen-like atoms. Thus the atomic states such as $2\ ^2S_{1/2}$ and $2\ ^2P_{1/2}$ are degenerate not only for the Schrödinger Hamiltonian but also in the relativistic Dirac theory.[28] This is in contradiction with experimental results and a great deal of theoretical work has been done to explain the level-shift in terms of corrections involving virtual photon processes.[26]

In what follows, we shall show by a simple perturbation calculation that on assuming a modified Coulomb potential for the electron-nucleus interaction of the form $-(Z/r)(1-e^{-\alpha_p e^r})$, the degeneracy is lifted by an appropriate magnitude. As the corrections are small, a perturbation calculation to first order seems to be adequate for a fairly accurate idea of the magnitude. For hydrogenic wave functions (radial part only) of the type,

$$_{nl}(r) = -\left[\frac{(2Z/n)^3(n-1-1)!}{2n[(n+1)!\ ]}\right]^{1/2} e^{-\rho/2} L_{n+1}^{2l+1}(\rho) \qquad (4.1)$$

with

$$\rho = \frac{2Z\ r}{n}$$

and

$L_{n+1}^{2l+1}(\rho)$ = associated Laguerre polynomials, where

n and l are respectively, the principal and the orbital quantum numbers.

The idea is to calculate the relative level shift

$$\Delta E(n) = \Delta E(n\ ^2S_{1/2}) - \Delta E(n\ ^2P_{1/2}), \qquad (4.2)$$

where the individual level shifts are given by

$$\Delta E(n\ ^2S_{1/2}) = \langle \Psi_{no}(r) \mid \Delta V(r) \mid \Psi_{no}(r) \rangle$$

and

$$\Delta E(n\ ^2P_{1/2}) = \langle \Psi_{nl}(r) \mid \Delta V(r) \mid \Psi_{nl}(r) \rangle .$$

The perturbation ΔV is given by the Yukawa part of the modified potential (2.4) that is

$$\Delta V(r) = +(Z/r)(e^{-\alpha_{pe} \cdot r}). \qquad (4.3)$$

Using the wave function (4.1) we get,

$$\langle \Psi_{nl}(r) \mid \Delta V(r) \mid \Psi_{nl}(r) \rangle$$

$$= \int_0^\infty \left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3} e^{-\rho} \rho^{2l} \left[L_{n+1}^{2l+1}(\rho) \right]^2 \frac{Z}{r} e^{-\alpha_{pe} r} r^2 dr$$

$$\cdots\cdots\cdots (4.4)$$

From (4.1) $\quad \rho = \dfrac{2Z}{n} r$

Hence

$$dr = \dfrac{n}{2Z} d\rho$$

Hence the equation (4.4) becomes

$$= \int_0^\infty \left(\dfrac{2Z}{n}\right)^3 \dfrac{(n-l-1)!}{2n[(n+1)!]^3} e^{-\rho} \rho^{2l} \times Z \times \dfrac{n}{2Z} \quad e^{-\alpha} \rho e^{\frac{n}{2Z}}$$

$$\times \; [\; L_{n+l}^{2l+1}(\rho)]^2 \; \dfrac{n}{2Z} \; d\rho \qquad\qquad (4.5)$$

$$= \dfrac{n^2}{4Z} \times \left(\dfrac{2Z}{n}\right)^3 \dfrac{(n-l-1)!}{2n[(n+1)!]^2}$$

$$\int_0^\infty \rho^{2l+1} \; e^{-(1+\frac{\alpha \rho e}{2Z})^n} \; [\; L_{n+l}^{2l+1}(\rho)]^2 \; d\rho . \qquad (4.6)$$

The associated Laguerre polynomial

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} \dfrac{(-1)^{k+1}[(n+1)!]^2}{(n-l-1-k)!(2l+1+k)!k!} \times \rho^k . \qquad (4.7)$$

Consider only the first term i.e. when $k = 0$

$$L_{n+l}^{2l+1}(\rho) = \dfrac{-[(n+1)!]^2}{(n-l-1)!(2l+1)!} . \qquad\qquad (4.8)$$

Hence

$$\left[L_{n+1}^{2l+1}(\rho) \right]^2 = \frac{[(n+1)!]^4}{[(n-l-1)!]^2 [(2l+1)!]^2} \cdot \tag{4.9}$$

Substituting this value in the equation (4.5) we get

$$\langle \Psi_{nl}(r) | \Delta V(r) | \Psi_{nl}(r) \rangle$$

$$= \frac{n^2}{4Z} \left(\frac{2Z}{3}\right)^3 \frac{(n-l-1)!}{2n[(n+1)!]^3} \frac{[(n+1)!]^4}{[(n-l-1)!]^2[(2l+1)!]^2}$$

$$x \int_0^\infty e^{-(1+ a_{pe}\frac{n}{2Z})} \rho^{2l+1} \, d\rho \tag{4.10}$$

$$= -\frac{n}{8Z} \left(\frac{2Z}{3}\right)^3 \frac{(n+1)!}{(n-l-1)![(2l+1)!]^2} \times \frac{(2l+1)!}{(1+a_{pe}\frac{n}{2Z})^{(2l+2)}} \tag{4.11}$$

$$= -\frac{n}{8Z} \left(\frac{2Z}{n}\right)^3 \frac{(n+1)!}{(n-l-1)!(2l+1)!} \times \frac{1}{(1+ \alpha_{pe}\frac{n}{2Z})^{(2l+2)}} \cdot \tag{4.12}$$

Now when $l = 0$, we get

$$\Delta E(n^2 S_{1/2}) = \frac{n}{8Z} \left(\frac{2Z}{n}\right)^3 \frac{n!}{(n-1)!} \times \frac{1}{(1+a_{pe}\frac{n}{2Z})^2}, \tag{4.13}$$

and when $l = 1$

$$\Delta E(n\,^2 P_{1/2}) = \frac{n}{8Z} \left(\frac{2Z}{n}\right)^3 \frac{(n+1)!}{(n-2)!x3!} \frac{1}{(1+a_{pe}\frac{n}{2Z})^4} \cdot \tag{4.14}$$

Hence the splitting from the first order perturbation

$$\Delta E(n) = \Delta E(n\,^2S_{1/2}) - \Delta E(n\,^2P_{1/2})$$

$$= \frac{n}{8Z}\left(\frac{2Z}{n}\right)^3 \times \frac{n}{(\;1)\alpha_{pe}\frac{n}{2Z})^2} - \frac{n}{8Z}\left(\frac{2Z}{n}\right)^3 \frac{(n-1)n(n+1)}{6(1+\alpha_{pe}\frac{n}{2Z})^4} \qquad (4.15)$$

As α_{pe} is expected to have a very large value ($\sim 10^3$), we have $\alpha_{pe} \gg 2Z/n$. Thus the second term of the equation (4.15) may be neglected since α_{pe} occurs in the fourth power in the denominator.

Thus the energy level shift becomes

$$\Delta E(n\,^2S_{1/2}) - \Delta E(n\,^2P_{1/2})$$

$$\simeq \frac{n}{8Z}\left(\frac{2Z}{n}\right)^3 \times \frac{n}{(1+\alpha_{pe}\frac{n}{2Z})^2} \qquad (4.16)$$

$$= \left(\frac{4Z^4}{n^3}\right)\left(\frac{1}{\frac{2Z}{n}+\alpha_{pe}}\right)^2 . \qquad (4.17)$$

Thus the shift is proportional to Z^4 for smaller values of Z but will change less rapidly for large values of Z. A similar conclusion was arrived at by Bethe[29] on the other grounds. Also the dependence on the principal quantum number n is of the inverse type, i.e. proportional to $1/n^3$.

A fairly close agreement with the experimental values of Lamb-shift for H and He$^+$ can be obtained on choosing the

value of α_{pe} of the order of the reciprocal of 2.9×10^{-12} cms
to 2.7×10^{-12} cms. However, in the absence of a precise
knowledge of the Z dependence of the parameter α_{pe}, it is much
more appropriate to compare the ratios of the Lamb-shift
values for different values of n for the same atom. These
theoretical ratios derived from (4.17) for H atom and the He^{+}
ion are set out in Table II along with the experimental ratios.
The agreement seems to be very good and well within experi-
mental tolerances given. Thus the present expression predicts
the right dependence on the principal quantum number. This
result is very suggestive and the modified potential seems to
take account of radiation corrections in a phenomenological
manner.

TABLE - II

Theoretical and Experimental Ratios of the
Lamb-Shifts for the various excited states
of H and He$^+$

System \ Ratio	$\Delta E(4)$	:	$\Delta E(3)$	:	$\Delta E(2)$
H (Experimental)	1	:	2.368	:	7.95
He$^+$(Experimental)	1	:	2.41	:	8.002
Theoretical	1	:	2.370	:	8

$$\Delta E(n) = \Delta E(n^2 S_{\frac{1}{2}}) - \Delta E(n^2 p_{\frac{1}{2}})$$

C H A P T E R - 5

DISCUSSION AND CONCLUSIONS

In the foregoing sections the question of spatial
correlation in two-electron atoms has been reconsidered in view
of the possible modification of the Coulomb law of interaction
of two point charges so as to remove the singularity of the
potential at the origin. This is based on the belief that
the physical laws of nature do not admit such singularities and,
as such, the latter must be regularised away in any physical
theory. Accordingly, the correlation error is attributed to
the divergent character of the Coulomb potential. For actual
calculation the modified Coulomb potential, as suggested by
Landé and Thomas,[23] is used in the form

$$V(r_{ij}) = \frac{e_i e_j}{r_{ij}} (1 - e^{-\alpha_c r_{ij}}). \tag{5.1}$$

In the absence of any objective criteria for determining the
cut-off parameter α_c, the latter was estimated from purely
heuristic considerations. It is found that much of the corre-
lation error could be accounted for in the case of the ground
state of the helium-like series from $Z = 1$ to $Z = 6$, if α_c is
chosen to be of the form $\alpha_c = 2Z^2$ (in atomic units). Only one-
parameter hydrogenic trial functions were used. Improvement in
each case was of the order of 0.04 a.u., which is substantial.

The removal of the accidental degeneracy in one-electron
hydrogen-like atoms, i.e. the phenomenon of Lamb-shift, was

interpreted in terms of the modified Coulomb potential. The Yukawa term occurring in the modified potential (5.1) causes a splitting of the otherwise orbitally degenerate states such as $2 \, ^2S_{1/2}$ and $2 \, ^2P_{1/2}$, thereby providing a natural explanation of the atomic fine-structure, i.e. the Lamb-shift. It was shown by a simple first order calculation treating the Yukawa term $- \frac{e_i e_i}{r_{ij}} e^{-\alpha_{pe} r_{ij}}$ as a small perturbation and using the unperturbed hydrogenic wave functions as the basis, that the energy splitting is given by

$$\Delta E(\gamma) \equiv \Delta E \, (n \, ^2S_{1/2}) - \Delta E \, (n \, ^2P_{1/2})$$

$$\simeq \left(\frac{4z^4}{n^3} \right) \left(\frac{1}{\frac{2z}{n} + \alpha_{pe}} \right)^2 . \tag{5.2}$$

Expression (5.2) has essentially the same form as of that obtained by Bethe[29] from the radiative correlation considerations. The splitting is found to be of the right sign and is inversely proportional to the third power of the principal quantum number n. Also it increases initially as z^4 and then less rapidly for large values of the nuclear charge number z. The first-order perturbation calculation is justified, in spite of the fact that the perturbation $- \frac{e_i e_i}{r_{ij}} e^{-\alpha_{pe} r_{ij}}$ diverges for r_{ij} tending to zero, as its matrix elements are finite and small compared to the spacing of different energy states. The inference that the modification phenomenologically takes into account the quantum-mechanical virtual photon processes is justified heuristically by series expanding the modified potential

$$V(r_{ij}) = \frac{e_i e_j}{r_{ij}} (1 - e^{-\alpha_c r_{ij}}) \qquad (5.3)$$

in the reciprocal space:

$$V(r_{ij}) = \frac{4\pi e_i e_j}{\Omega} \sum_{k} (\frac{1}{k^2} - \frac{1}{k^2 + \alpha_c^2}) e^{-i\underline{k}\cdot\underline{r}_{ij}}, \qquad (5.4)$$

which is, aside from a factor 1/2 occassioned by spin considerations, strongly reminiscent of the screened potential obtained by Hubbard[25] from a many-body theoretic treatment. Thus the second term in (5.3) and (5.4) represents polarization effects similar to those involved in virtual photon process.

Unfortunately, there appears to be no a'priori criterion for ascertaining α_c. However, a order-of-magnitude agreement with experimental results is obtained for α_c lying in the expected range, i.e. in the neighbourhood of the reciprocal of the electron Compton wave length.[24]

The plausibility of the modified Coulomb potential, on which the preceeding chapters are predicated, appears to be reiterated from several independent viewpoints. The formal similarity (made all the more evident in the reciprocal space) with the screened many-body potential of Hubbard (cf.eqn.(5.4)) leads to an interpretation of α_c as a cut-off wave-vector magnitude associated with the virtual photon processes.

A still novel interpretation of the modified Coulomb law can be had in terms of a stochastic process envisaged by some

authors,[30] in the context of potential scattering, where the
spherically symmetrical potential was allowed to evolve
stochastically with the radial distance. Such a spherically
symmetric potential is given by

$$V(r_{12}) = \mu / r_{12}, \tag{5.5}$$

where the parameter μ is a stochastic variable evolving with
the radial distance r_{12}. Assuming a binary Markovian process
($\mu = +1$, or -1) for the variate μ , the average potential
was found to be given by

$$V_{av}(r_{12}) = \frac{(q - p + 2p\, e^{-\lambda r_{12}})}{\lambda\, r_{12}}, \tag{5.6}$$

where $\lambda = p + q$, p is the probability per unit distance that
μ jumps from +1 to -1, and q the probability of the comple-
mentary event. Also, for the case $\mu = 1$, or 0, the above
expression is modified as

$$V_{av}(r_{12}) = \frac{(q + pe^{-\lambda r_{12}})}{\lambda\, r_{12}} \tag{5.7}$$

The above two potential are readily seen to be linear combi-
nations of the Coulomb and the Yukawa potentials. With the
proper choice of the probability densities p and q, the above
expressions can be shown to be equivalent to the modified
potential (5.1) employed in the proceeding calculations.

The stochastic nature of the charge parameter μ , however
renders the usual charge conservation law statistical in

character. As is well-known, the charge conservation is associated with, in fact consequent upon, the gauge invariance of the first kind.[31] The above would imply that the gauge invariance of the first kind holds only in the statistical sense. The violation of this gauge invariance, of course, should lead to creation or annihilation of electrical charges. This would suggest the occurrence of some short lived (exchange) particles which are presumably responsible for the modification of the Coulomb law. The above explanation, though fascinating, can at best be regarded as purely suggestive, and is, of course, not essential to the present thesis.

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