

AN APPROXIMATE METHOD FOR THREE-BODY BOUND
ATOMIC SYSTEMS

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By

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ABSTRACT

The Feshbach-Rubinow approximation which is one of the many approximate methods to solve three-body problems was first applied to the triton problem. In this approximation, the three-body problem is reduced to an equivalent two-body problem and the total three-body wavefunction is assumed to depend on a single non-negative variable. The problem then reduces to the solving of a single second order differential equation. When this approximation is made in the atomic three-body problem of the helium atom and helium-like ions, the Schrödinger-like equation that is obtained is analytically solvable, yielding reasonable results for the ground-state energy. Calculations have previously been done with just one variational parameter in the variable on which the wavefunction depends. In this thesis, the definition of the variable has been modified on physical grounds to take better account of screening, and contains two variational parameters. Analytic solutions of the differential equation can again be found, and improved numerical results are obtained. These are compared with the results obtained from the more elaborate K-harmonics approach.

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CHAPTER I
INTRODUCTION

The three-body problem has been of interest to physicists long before the beginning of the quantum era. The problem of paths followed by two planets on their passage around the sun is one of many examples. In quantum mechanics, the three-body problem has enjoyed great popularity among the physicists over the last few decades.

In this thesis, we deal with the atomic three-body problem of two electrons and a nucleus, as in the helium atom or helium-like ions. When one speaks of the three-body problem, the first characteristic that comes to mind is its "insolubility". In atomic domain this describes, for instance, the situation for the helium atom whose Schrödinger equation does not admit of an exact solution as in the corresponding hydrogen atom problem. This feature of insolubility is intimately connected with the very law of force - the coulomb force - which so accurately describes the behaviour of atomic systems. Therefore the best a physicist can do with atomic three-body systems is to devise powerful approximation techniques to obtain numerically accurate results for comparison with experimental data. An excellent review of the work done upto 1956 is due to Bethe and

Salpeter [1]. Starting from the non-relativistic equation for helium-like systems there has been a long sequence of calculations on the bound states of these systems, culminating in the work of Pekeris [2] which has yielded eigenvalues accurate up to 10 or 11 significant figures.

Basically two approaches have been attempted to solve the problem of helium-like systems. The variational technique consists of choosing a trial function ψ_t containing a number of variational parameters which are varied to minimise the quantity $E_t = \langle \psi_t | H | \psi_t \rangle$ with $\langle \psi_t | \psi_t \rangle$ finite, where H is the Hamiltonian of the system. Depending upon the flexibility of ψ_t , E_t can be very close to the true energy E . On the other hand, in the K-harmonics approach, the relative motion of the three-body system is described by a Schrödinger-like equation in six-dimensional space. The two-body potential is expressed in terms of generalised angular momentum eigenfunctions for the three body system and one finally gets an infinite set of coupled differential equations.

The approximation method that we have used here is a variational approach and was first applied in nuclear physics by Feshbach and Rubnow. In this method one assumes that the total three-body wave function depends on a single non-negative symmetric variable. We have given a brief account of this method [3] and its generalization [4] in chapter II.

In chapter III, the method has been applied to a model one dimensional helium-like system with zero range forces and

it is found that the estimates on the ground state energy are better compared to those obtained from other simple approximate methods [6,7,8]. The Feshbach-Rubinow method has been then shown to give still better results by a more judicious choice of the variable on which the wave function depends.

The ground state energy of realistic two-electron atomic systems has been determined by the modified Feshbach-Rubinow method and the results compared with those of Pekeris [2] and Bhaduri et al. [10] in chapter IV. It is seen that the analytic solutions for the ground state energy and wave function are obtained. Despite the minimal computational work involved, the modified Feshbach-Rubinow approximation gives fairly good results.

CHAPTER II

THE FESHBACH-RUBINOW METHOD

We have applied the Feshbach-Rubinow (FR) method to three-body atomic systems like H^- , He, Li^+ , Be^{++} etc. to calculate the ground state energy of these systems. It is worthwhile, therefore, to give here a brief account of the method although results of the FR and the generalised FR methods have been given in ref. [3] and [4] respectively.

In the FR method, the three-body problem is reduced to an equivalent two-body problem using variational principle. The two-body forces are assumed to be central and the total three-body wavefunction spherically symmetric. It is assumed at the outset that the three-body wavefunction is a function of a single symmetric variable which leads to a second order differential equation similar to the Schrödinger equation for deuteron. The lowest eigenvalue of the obtained two-body equation is an upperbound of the ground state energy of the original three-body system. Feshbach and Rubinow [3] applied this method in the case of triton assuming all three particles to have the same mass interacting with identical pair-wise nuclear force.

The Hamiltonian H for a three-body system in any

reference frame is

$$H = -\frac{\hbar^2}{2} \sum_{i=1}^3 \frac{1}{m_i} \nabla_i^2 + \sum_{i<j} v(|\underline{x}_i - \underline{x}_j|)$$

where \underline{x}_i and m_i are the position vector and the mass of the i th particle.

The centre of mass motion of the system being removed, the Hamiltonian H in the relative coordinates is given by

$$H = \sum_{\text{cyclic}} \left[-\frac{\hbar^2}{2} \left\{ \left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) + \frac{1}{m_1} \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \frac{\partial^2}{\partial r_2 \partial r_3} \right\} + v_1(r_1) \right] \quad (2.1)$$

where r_1 is the distance between particles 2 and 3 and so on for r_2 and r_3 .

For a system of particles with equal mass m , eqn. (2.1) reduces to

$$H = \sum_{\text{cyclic}} \left[-\frac{\hbar^2}{m} \left\{ \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{r_2^2 + r_3^2 - r_1^2}{2r_2 r_3} \frac{\partial^2}{\partial r_2 \partial r_3} \right\} + v_1(r_1) \right] \quad (2.2)$$

The Schrödinger equation

$$H\psi = E\psi$$

can then be written for convenience in the following variational form

$$\begin{aligned}
0 = & \delta \int_0^\infty dr_1 \int_0^{r_1+r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_3 r_1 r_2 r_3 \\
& \times \left[\left(\frac{\partial \psi}{\partial r_1} \right)^2 + \left(\frac{\partial \psi}{\partial r_2} \right)^2 + \left(\frac{\partial \psi}{\partial r_3} \right)^2 \right. \\
& + \frac{r_1^2 + r_2^2 - r_3^2}{2r_1 r_2} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_2} + \frac{r_2^2 + r_3^2 - r_1^2}{2r_2 r_3} \frac{\partial \psi}{\partial r_2} \frac{\partial \psi}{\partial r_3} \\
& + \frac{r_3^2 + r_1^2 - r_2^2}{2r_3 r_1} \frac{\partial \psi}{\partial r_3} \frac{\partial \psi}{\partial r_1} \\
& \left. + \frac{m}{\hbar^2} \{v_1(r_1) + v_2(r_2) + v_3(r_3)\} \psi^2 - \frac{m}{\hbar^2} E \psi^2 \right] \quad (2.3)
\end{aligned}$$

where E is the centre of mass energy of the system.

Since only S-states are considered, the wavefunction ψ is a function of r_1 , r_2 and r_3 only. The wavefunction is symmetric under the exchange of any two particles and is normalized as

$$\int_0^\infty dr_1 \int_0^{r_1+r_2} dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_3 r_1 r_2 r_3 |\psi(r_1, r_2, r_3)|^2 = 1.$$

Feshbach and Rubirow chose the functional form of ψ to depend only on a single symmetric non-negative variable R such that

$$\psi = \phi(R)$$

$$R = \frac{1}{2}(r_1 + r_2 + r_3)$$

where ϕ is an unknown arbitrary function of the perimeter of the triangle formed by the three particles. Thus, changing

the variables so that R becomes one of the independent variables

$$\begin{aligned}
 R &= \frac{1}{2}(r_1 + r_2 + r_3) \\
 R_2 &= r_2 \\
 R_3 &= r_3
 \end{aligned}$$

the volume integral becomes

$$\begin{aligned}
 &\int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_3 r_1 r_2 r_3 \\
 &= 2 \int_0^\infty dR \int_0^R dR_2 \int_{R-R_2}^R dR_3 (2R-R_2-R_3) R_2 R_3 \\
 &\approx \frac{7}{30} \int_0^\infty R^5 dR \tag{2.4}
 \end{aligned}$$

The integration over R_2 and R_3 is easily performed and eqn. (2.3) reduces to

$$0 = \delta \int_0^\infty dR \frac{R^5}{8} \left[\left(\frac{d\phi}{dR} \right)^2 + \frac{m}{\hbar^2} V_{\text{eff}} \phi^2 - \frac{m}{\hbar^2} \frac{14}{15} E \phi^2 \right] \tag{2.5}$$

where

$$V_{\text{eff}} = \frac{8}{R^5} \int_0^R dR_2 \int_{R-R_2}^R dR_3 (2R-R_2-R_3) R_2 R_3 [v_1(r_1) + v_2(r_2) + v_3(r_3)]. \tag{2.6}$$

For a potential of the shape $v_i(r_i) = V_i v(r_i)$ with V_i constant, V_{eff} can be simplified, by cyclic permutation of variables, and written as

$$V_{\text{eff}} = (V_1 + V_2 + V_3) \frac{8}{R^5} \int_0^R dR_2 (R^2 R_2^2 - R R_2^3 + \frac{1}{6} R_2^4) v(R_2) \quad (2.7)$$

Subsequent use of the Euler-Lagrange equation to eqn. (2.5) yields the differential equation

$$\frac{1}{R^5} \frac{d}{dR} (R^5 \frac{d\phi}{dR}) - \frac{14}{15} k^2 \phi + U_{\text{eff}} \phi = 0 \quad (2.8)$$

where $k^2 = \frac{m}{\hbar^2} |E|$ and $U_{\text{eff}} = -\frac{m}{\hbar^2} V_{\text{eff}}$. For the bound state problem, $|E| = -E$.

Making the substitution $F(R) = \phi(R) R^{5/2}$, eqn. (2.8) becomes

$$\frac{d^2 F}{dR^2} - \frac{14}{15} k^2 F - \frac{15}{4} \frac{1}{R^2} F + U_{\text{eff}} F = 0 \quad (2.9)$$

Since eqn. (2.9) is obtained from variational principle, its solution gives the best function depending solely on R . This equation is similar to the Schrödinger equation for the deuteron. It has an effective mass of $\frac{14}{15} m$ and a centrifugal potential energy term $\frac{15}{4} R^{-2}$ corresponding to orbital angular momentum quantum number $\ell = 3/2$. It should be noted that the centrifugal term arises from the kinetic energy terms in the Hamiltonian, irrespective of the choice of the two-body potential. The term U_{eff} is an averaged potential given by eqn. (2.6). The term $\frac{15}{4} R^{-2} - U_{\text{eff}}$ may be called the true effective potential of the problem.

A very important property of V_{eff} is worth mentioning here. From an inspection of eqn. (2.7) one can say that

if the two-body potential $v(R_2)$ is a polynomial of order n in R_2 , then V_{eff} will also be a polynomial of same order in R . The same result holds for two-body potentials of the type $\frac{1}{R^n}$ and in particular the coulomb potential which goes as $\frac{1}{R}$. This is interesting since in the three-body atomic systems where the pair-wise force is coulombic in nature, V_{eff} will be a coulomb potential. Eqn. (2.9) will then take the form of Schrödinger equation for hydrogen-like systems with $\ell = 3/2$, solutions of which are known analytically..

Referring to eqn. (2.9) one sees that the task of finding an appropriate S-state wavefunction is reduced to solving the equation. The FR method has the advantage of connecting directly the S-state wavefunction to the two-body potential. Thus the potential being once chosen, the wavefunction is uniquely determined.

One should also note the circumstances where the FR method is expected to work well. The method treats equally all possible configurations having the same value of R , independent of the choice of potential. However, it can be easily seen that for a two body potential with a short range part followed by an attractive part, the method will not be satisfactory since a configuration with two particles close together experiencing repulsion and the third particle far away is clearly not the same as a configuration in which all the three particles interact via attractive force. Thus, for the FR method to give good results it is necessary that the

two-body potential be a smoothly varying function of the inter-particle distance, so that all the particles experience the same type of force in all configurations. This condition is very well satisfied in atomic systems and therefore one may be tempted to apply this method to such systems.

Generalised FR Method

The FR method can be generalised [4] to take into account the three body systems in which the particles have different masses and the two-body forces are different but central. Mathematical details are given in the Appendix. The wavefunction ψ is still a function of a single variable R containing a few variational parameters. R is now defined in such a way so as to take into account different interactions.

$$\psi = \phi(R)$$

$$R = \frac{1}{2} (\eta_1 r_1 + \eta_2 r_2 + \eta_3 r_3) \quad (2.10)$$

where η_1, η_2, η_3 are variational parameters. These are a measure of relative strengths of the three two-body interactions and the asymmetry in the masses of the particles. Since r_1, r_2, r_3 and hence R are non-negative quantities, the triangular conditions $r_1 + r_2 > r_3$ etc. restrict the possible values of η 's such that $\eta_1 + \eta_2 > 0, \eta_2 + \eta_3 > 0$ and $\eta_3 + \eta_1 > 0$. For example, using the condition $r_1 + r_2 > r_3$, one has

$$0 \leq 2R < [(\eta_1 + \eta_3)r_1 + (\eta_2 + \eta_3)r_2]$$

It follows that for all possible values of r_1 and r_2 ranging from 0 to ∞ , the above condition is satisfied only for $\eta_1 + \eta_3 > 0$ and $\eta_2 + \eta_3 > 0$.

Proceeding the same way as the original FR method, one finally obtains the differential equation

$$-\frac{\hbar^2}{m} \frac{d^2 F}{dR^2} + V(R)F = 8\xi EF \quad (2.11)$$

where

$$F(R) = R^{5/2} \phi(R)$$

$$\frac{1}{m} = \xi \sum_{\text{cyclic}} (\eta_1^2 + \eta_2^2) \frac{1}{m_3} + \zeta \eta_1 \eta_2 \eta_3 \sum_{i=1}^3 \left(\frac{1}{m_i} \right) \quad (2.12)$$

$$V(R) = \frac{\hbar^2}{m} \frac{15}{4R^2} + 4 \sum_{i=1}^3 W_i(R) \quad (2.13)$$

The quantities ξ , ζ , $W_i(R)$ are defined as follows.

$$\int (dr) r_1 r_2 r_3 = 2\xi \int_0^\infty R^5 dR$$

$$\int (dr) r_1 (r_2^2 + r_3^2 - r_1^2) = 2\eta_1 \zeta \int_0^\infty R^5 dR$$

$$\int (dr) r_1 r_2 r_3 v_1(r_1) = \int_0^\infty R^5 W_1(R) dR$$

$$\int (dr) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_3$$

Explicit forms for ξ , ζ and $W_i(R)$ are as follows

$$\xi = \frac{2^5 \{ (\eta_1 + \eta_2 + \eta_3)^3 + \eta_1 \eta_2 \eta_3 \}}{15 \{ (\eta_1 + \eta_2) (\eta_2 + \eta_3) (\eta_3 + \eta_1) \}^3} \quad (2.14)$$

$$\zeta = \frac{2^6 \{ (\eta_1 + \eta_2 + \eta_3)^2 + \eta_1 \eta_2 + \eta_2 \eta_3 + \eta_3 \eta_1 \}}{15 \{ (\eta_1 + \eta_2) (\eta_2 + \eta_3) (\eta_3 + \eta_1) \}^3} \quad (2.15)$$

$$\begin{aligned} W_1(R) = & \frac{4}{3(\eta_2 + \eta_3)^3} \left[\int_0^{2/(\eta_3 + \eta_1)} dt \{ 12 - 12\eta_1 t + (3\eta_1^2 - \eta_2 \eta_3) t^2 \} t^2 v_1(Rt) \right. \\ & + \frac{\eta_3}{(\eta_2 - \eta_3)^3} \int_{2/(\eta_3 + \eta_1)}^{2/(\eta_1 + \eta_2)} dt \{ 32\eta_2 - 12(\eta_3^2 + 4\eta_1 \eta_2 + 3\eta_2^2) t \\ & + 12(\eta_1 + \eta_2)(\eta_3^2 + 2\eta_1 \eta_2 + \eta_2^2) t^2 \\ & \left. - (\eta_1 + \eta_2)^2 (3\eta_3^2 + 4\eta_1 \eta_2 + \eta_2^2) t^3 \} t v_1(Rt) \right]. \quad (2.16) \end{aligned}$$

The η 's appear in above expressions in such a way that cyclic permutation of these parameters leaves ξ , ζ and $\Sigma W_i(R)$ unchanged as expected, since R_1, R_2 and R_3 are cyclic variables.

It may be mentioned that the FR method was generalized by Abou-Hadid and Higgins [5] for the case where two of the particles are considered identical and applied to ${}^3_{\Lambda}$ system. All the expressions in ref [4] reduce to the corresponding expressions in ref [5] for $\eta_1 = \eta_2 = 1$ and $\eta_3 = \eta$.

CHAPTER III

ONE DIMENSIONAL HELIUM-LIKE SYSTEMS

One dimensional problems are useful not only because of the simple mathematics involved but also because of the physical insight provided which helps one to probe into realistic three-body problems. One dimensional three-body problems have been studied by several authors. It is known that the exact solutions cannot be obtained analytically for such systems except for the special case of three particles of equal mass interacting via attractive zero-range interparticle potentials of equal strength [9]. The three-body systems must, therefore, be studied by approximate methods such as perturbation theory, variational method and the Hartree-Fock approximation. These techniques have been applied [6, 7, 8] to a model one dimensional helium-like system interacting via delta function potential. We have applied here the FR approximation to such a model system. It turns out that the corresponding solutions are simple and the ground state energy is lower than previous results. This suggests that the FR method can yield still better results if the definition of the variable R in the wavefunction is suitably modified, which we have done by taking into account the screening of the nucleus by the electrons. We have found that the ground state energy is further lowered.

In this chapter, we first use the FR approximation to get an equivalent two-body differential equation for a three-body system with unequal masses and interacting via central forces. The validity of the equation is then checked by applying it to a special case for which the ground state energy is exactly known. We then proceed to calculate the ground state energy of the helium-like atom by FR and the modified FR approximations.

The kinetic energy operator T' in a reference frame is

$$T' = -\frac{\hbar^2}{2} \sum_{i=1}^3 \frac{1}{m_i} \frac{\partial^2}{\partial x_i^2}, \quad (3.1)$$

where x_i and m_i are the position vector and mass of the i th particle.

The centre of mass motion being removed, the kinetic energy operator T in relative coordinates is

$$T = -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_1^2} + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_2^2} - \frac{2}{m_3} \frac{\partial^2}{\partial r_1 \partial r_2} \right] \quad (3.2)$$

where $r_1 = x_2 - x_3$, $r_2 = x_3 - x_1$ and $r_3 = x_1 - x_2$.

There are three possible geometries, depending upon which particle is positioned in between the other two. The corresponding expressions for T are not the same.

a) $r_3 = r_1 + r_2$

$$T = -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_1^2} + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_2^2} - \frac{2}{m_3} \frac{\partial^2}{\partial r_1 \partial r_2} \right] \quad (3.3)$$

$$b) \quad r_3 = r_2 - r_1$$

$$T = -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_1^2} + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_2^2} + \frac{2}{m_3} \frac{\partial^2}{\partial r_1 \partial r_2} \right] \quad (3.4)$$

$$c) \quad r_3 = r_1 - r_2$$

$$T = -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_1^2} + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_2^2} + \frac{2}{m_3} \frac{\partial^2}{\partial r_1 \partial r_2} \right]. \quad (3.5)$$

The Schrödinger equation for the system can be written in the variation form

$$\begin{aligned} 0 = & \delta \int_0^\infty dr_1 \left[\int_0^\infty dr_2 \left\{ -\frac{\hbar^2}{2} \left\{ \left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial \psi}{\partial r_1} \right)^2 + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) \left(\frac{\partial \psi}{\partial r_2} \right)^2 \right. \right. \right. \\ & \left. \left. \left. - \frac{2}{m_3} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_2} \right\} - \{v_1(r_1) + v_2(r_2) + v_3(r_3)\} \psi^2 + E\psi^2 \right\} \right. \\ & \left. + \int_0^\infty dr_2 \left\{ -\frac{\hbar^2}{2} \left\{ \left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial \psi}{\partial r_1} \right)^2 + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) \left(\frac{\partial \psi}{\partial r_2} \right)^2 + \frac{2}{m_3} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_2} \right\} \right. \right. \\ & \left. \left. - \{v_1(r_1) + v_2(r_2) + v_3(r_3)\} \psi^2 + E\psi^2 \right\} \right. \\ & \left. + \int_0^\infty dr_2 \left\{ -\frac{\hbar^2}{2} \left\{ \left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial \psi}{\partial r_1} \right)^2 + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) \left(\frac{\partial \psi}{\partial r_2} \right)^2 + \frac{2}{m_3} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_2} \right\} \right. \right. \\ & \left. \left. - \{v_1(r_1) + v_2(r_2) + v_3(r_3)\} \psi^2 + E\psi^2 \right\} \right] \quad (3.6) \end{aligned}$$

Defining new variables

$$R = \frac{1}{2}(\eta_1 r_1 + \eta_2 r_2 + \eta_3 r_3) \quad (3.7)$$

$$R_2 = r_2$$

and choosing the wavefunction ψ to be of the form

$$\psi = \phi(R)$$

one can write eqn (3.6) as

$$\begin{aligned} 0 = & \delta \int_0^\infty dR \left[\frac{2}{\eta_1 + \eta_3} \int_0^{2R/(\eta_2 + \eta_3)} dR_2 \{ A \left(\frac{d\phi}{dR} \right)^2 - (v_1 + v_2 + v_3) \phi^2 + E \phi^2 \} \right. \\ & + \frac{2}{\eta_1 - \eta_3} \int_{2R/(\eta_1 + \eta_2)}^{2R/(\eta_2 + \eta_3)} dR_2 \{ B \left(\frac{d\phi}{dR} \right)^2 - (v_1 + v_2 + v_3) \phi^2 + E \phi^2 \} \\ & \left. + \frac{2}{\eta_1 + \eta_3} \int_0^{2R/(\eta_1 + \eta_2)} dR_2 \{ C \left(\frac{d\phi}{dR} \right)^2 - (v_1 + v_2 + v_3) \phi^2 + E \phi^2 \} \right] \quad (3.8) \end{aligned}$$

where

$$A = -\frac{\hbar^2}{8} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) (\eta_1 + \eta_3)^2 + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) (\eta_2 + \eta_3)^2 - \frac{2}{m_3} (\eta_1 + \eta_3) (\eta_2 + \eta_3) \right]$$

$$B = -\frac{\hbar^2}{8} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) (\eta_1 - \eta_3)^2 + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) (\eta_2 + \eta_3)^2 + \frac{2}{m_3} (\eta_1 - \eta_3) (\eta_2 + \eta_3) \right]$$

$$C = -\frac{\hbar^2}{8} \left[\left(\frac{1}{m_2} + \frac{1}{m_3} \right) (\eta_1 + \eta_3)^2 + \left(\frac{1}{m_1} + \frac{1}{m_3} \right) (\eta_2 - \eta_3)^2 + \frac{2}{m_3} (\eta_1 + \eta_3) (\eta_2 - \eta_3) \right]$$

Since ϕ , $\frac{d\phi}{dR}$ and E are independent of R_2 , integration over R_2 can be performed for integrands containing these terms in eqn. (3.8). One then gets

$$\begin{aligned}
0 = & \delta \int_0^{\infty} dR \left\{ R \left\{ \frac{G}{D} \left(-\frac{\hbar^2}{2} \right) \left(\frac{d\psi}{dR} \right)^2 + E \psi^2 \right\} \right. \\
& - \frac{1}{D} \left\{ \frac{2}{\eta_1 + \eta_3} \int_0^{2R/(\eta_2 + \eta_3)} dR_2 + \frac{2}{\eta_1 - \eta_3} \int_{2R/(\eta_1 + \eta_2)}^{2R/(\eta_2 + \eta_3)} dR_2 \right. \\
& \left. \left. + \frac{2}{\eta_1 + \eta_3} \int_0^{2R/(\eta_1 + \eta_2)} dR_2 \right\} \{ v_1(r_1) + v_2(r_2) + v_3(r_3) \} \psi^2 \right\} \quad (3.9)
\end{aligned}$$

where

$$D = 8(\eta_1 + \eta_2 + \eta_3) / [(\eta_1 + \eta_2)(\eta_2 + \eta_3)(\eta_3 + \eta_1)] \quad (3.10)$$

$$\begin{aligned}
G = & \frac{2}{(\eta_1 + \eta_2)(\eta_2 + \eta_3)(\eta_3 + \eta_1)} \left[\frac{1}{m_1} (\eta_2 + \eta_3) \{ (\eta_1 + \eta_2 + \eta_3)(\eta_2 + \eta_3) - 2\eta_2\eta_3 \} \right. \\
& + \frac{1}{m_2} (\eta_1 + \eta_3) \{ (\eta_1 + \eta_2 + \eta_3)(\eta_1 + \eta_3) - 2\eta_1\eta_3 \} \\
& \left. + \frac{1}{m_3} (\eta_1 + \eta_2) \{ (\eta_1 + \eta_2 + \eta_3)(\eta_1 + \eta_2) - 2\eta_1\eta_2 \} \right] \quad (3.11)
\end{aligned}$$

Note that D and G are symmetric in η 's and m 's.

Defining

$$\frac{1}{M} = \frac{G}{D} \quad (3.12)$$

$$\begin{aligned}
V_{\text{eff}} = & \frac{1}{DR} \left[\frac{2}{\eta_1 + \eta_3} \int_0^{2R/(\eta_2 + \eta_3)} dR_2 + \frac{2}{\eta_1 - \eta_3} \int_{2R/(\eta_1 + \eta_2)}^{2R/(\eta_2 + \eta_3)} dR_2 \right. \\
& \left. + \frac{2}{\eta_1 + \eta_3} \int_0^{2R/(\eta_1 + \eta_2)} dR_2 \right] \{ v_1(r_1) + v_2(r_2) + v_3(r_3) \} \quad (3.13)
\end{aligned}$$

where M is the effective mass of the system, one has

$$0 = \delta \int_0^{\infty} R \, dR \left[-\frac{\hbar^2}{2M} \left(\frac{d\phi}{dR} \right)^2 + E\phi^2 - V_{\text{eff}}\phi^2 \right].$$

Using Euler-Lagrange equation, the Schrödinger equation for the system is obtained

$$-\frac{\hbar^2}{2M} \frac{1}{R} \frac{d}{dR} \left(R \frac{d\phi}{dR} \right) + V_{\text{eff}}\phi - E\phi = 0.$$

Substituting $F(R) = R^{1/2}\phi(R)$, the above equation reduces to

$$-\frac{\hbar^2}{2M} \left[\frac{d^2 F}{dR^2} + \frac{1}{4R^2} F \right] + V_{\text{eff}} F = E F. \quad (3.14)$$

The centrifugal term $(-\frac{1}{4} R^{-2})$ in the above equation corresponds to orbital quantum number $\ell = -\frac{1}{2}$.

As a check to eqn. (3.14), we apply it to a system of three particles with same mass m and interacting via attractive interparticle delta function potentials of equal strength. Eqn. (3.14) then has exact solution. This system has been solved previously [9].

The effective mass M and V_{eff} from eqns. (3.12), and (3.13) are then

$$M = \frac{m}{2}$$

$$V_{\text{eff}} = -\frac{e^2}{R}$$

where e denotes the strength of the interparticle force. The Schrödinger equation (3.14) reduces to

$$-\frac{\hbar^2}{2m} \left[\frac{d^2 F}{dR^2} + \frac{1}{4R^2} F \right] - \frac{e^2}{2R} F = \frac{1}{2} E F.$$

This is just the wave equation for a coulomb potential for an effective orbital momentum state $l = -\frac{1}{2}$. The corresponding ground state energy E_0 in atomic units of me^4/\hbar^2 is -1 , which checks with the value obtained by McGuire [9]. The unnormalised ground state wavefunction is

$$\phi_0 = \exp(-R/2a)$$

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

We now apply the FR approximation to a simple one dimensional model of helium-like systems where the three particles interact via zero range interparticle potentials. The nuclear charge is Ze where $-e$ is the charge of an electron. The mass of the nucleus is assumed to be infinite, although the finite mass of nucleus can be easily taken into account. The Hamiltonian H in relative coordinates is

$$H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) - Ze^2 \{ \delta(x_1) + \delta(x_2) \} + e^2 \delta(x_1 - x_2). \quad (3.15)$$

Here x_1 and x_2 are the distances of the two electrons from the stationary nucleus at origin. The Schrödinger equation in variational form is

$$0 = \delta \int dx_1 dx_2 \left[\frac{\hbar^2}{2m} \left\{ \left(\frac{\partial \psi}{\partial x_1} \right)^2 + \left(\frac{\partial \psi}{\partial x_2} \right)^2 \right\} - Ze^2 \{ \delta(x_1) + \delta(x_2) \} \psi^2 + e^2 \delta(x_1 - x_2) \psi^2 - E \psi^2 \right]. \quad (3.16)$$

Since two of the three interparticle potentials are of the same type, the wavefunction ψ is chosen to be of the

form

$$\psi = \phi(R)$$

$$R = \frac{1}{2}(r_1 + r_2 + \eta r_3) \quad (3.17)$$

where η is a variational parameter. Here r_1 is the distance between particles 2 and 3 i.e. $r_1 = |x_1|$. Similarly $r_2 = |x_2|$ and $r_3 = |x_1 - x_2|$. Since R is a non-negative variable, the geometry of the system restricts the possible values of η such that $(1+\eta) \geq 0$.

The effective mass M defined in eqn (3.12) is

$$\frac{1}{M} = \frac{1+\eta}{2+\eta} \frac{(\eta^2 + \eta + 2)}{2m} \quad (3.18)$$

where m is the mass of an electron.

V_{eff} defined in eqn (3.13) is

$$\begin{aligned} V_{\text{eff}} &= -\frac{(1+\eta)^2 e^2}{4(2+\eta)R} \left[\frac{2}{(1+\eta)} \int_0^{2R/(1+\eta)} dR_2 + \frac{2}{(1-\eta)} \int_R^{2R/(1+\eta)} dR_2 \right. \\ &\quad \left. + \frac{2}{(1+\eta)} \int_0^R dR_2 \right] \{ Z\delta(r_1) + Z\delta(r_2) - \delta(r_3) \} \\ &= -\frac{e^2}{R} \frac{(1+\eta)(4Z-\eta-1)}{4(2+\eta)} \quad (3.19) \end{aligned}$$

Note that zero-range potentials give rise to V_{eff} which is coulombic in nature.

The Schrödinger equation for the system, using eqns (3.14), (3.18) and (3.19), becomes

$$-\frac{\hbar^2}{2m} \left(\frac{d^2 F}{dR^2} + \frac{1}{4R^2} F \right) - \frac{e^2}{R} \frac{4Z-n-1}{2(\eta^2+n+2)} F = \frac{2(2+n)}{(1+n)(\eta^2+n+2)} EF \quad (3.20)$$

This is the radial coulomb equation with centrifugal term corresponding to orbital quantum number $\ell = -\frac{1}{2}$. The ground state energy E_0 corresponding to principle quantum number $n = \frac{1}{2}$ can then be easily written in atomic units as

$$E_0 = - \frac{1+n}{(1+\frac{n}{2})} \frac{(Z - \frac{n}{4} - \frac{1}{4})^2}{(1 + \frac{n}{2} + \frac{n^2}{2})} \quad (3.21)$$

The ground state unnormalised wavefunction is

$$\phi_0(R) = \exp\left[-\frac{R}{a} \frac{(Z - \frac{n}{4} - \frac{1}{4})}{(1 + \frac{n}{2} + \frac{n^2}{2})}\right] \quad (3.22)$$

where $a = \hbar^2/me^2$ is the Bohr radius. While normalising the wavefunction one should note that

$$\int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 = \frac{8(\eta+2)}{(\eta+1)^2} \int_0^{\infty} R dR$$

For $\eta=0$, E_0 in eqn (3.21) reduces to $-(Z - \frac{1}{4})^2$ which is just the one parameter variational result [6]. For a given Z , eqn (3.21) should be minimised by varying η between -1 and ∞ . The ground state energy for different Z obtained from various approximations is compared in table 1. It is found that the FR method gives a lower value of E_0

than other estimates. A non-zero value of η in the wavefunction takes into account the interelectronic correlations and thus gives better result. This encourages one to apply the FR method with modification invoked in the wavefunction.

Although the smallest realistic nuclear charge Z is 1, it might be interesting to see how the three-body binding energy varies as Z is further reduced. Physically, one can see that as Z is reduced gradually, the three body binding energy becomes smaller and smaller due to the decrease in the total attractive coulomb force and hence an increase in the effect of repulsive force between the electrons. A point comes where the three-body binding energy becomes less than the binding energy of the two-body system of the nucleus and an electron interacting via attractive potential. The three body system is then no longer stable and it decays into the more stable two-body configuration and an electron. The ground state energy for a one-dimensional hydrogen-like system with attractive delta potential $-Ze^2\delta(x)$ is $Z^2/2$ in atomic units. The critical value Z_c of the nuclear charge at which the helium-like system is just no longer stable has been calculated from perturbation [6], variational [6], Hartree-Fock [7] and FR methods and are given in table 2. The ground state energy calculated by these methods is

$$E_{\text{per}} = - \left(Z^2 - \frac{Z}{2} \right)$$

$$E_{\text{var}} = - \left(Z - \frac{1}{4} \right)^2$$

$$E_{\text{HF}} = - \left(Z^2 - \frac{Z}{2} + \frac{1}{12} \right)$$

in atomic units. The perturbation and HF calculations are valid for $Z > \frac{1}{2}$, whereas the variational calculation is valid for $Z > \frac{1}{4}$. The FR approximation gives lower value of Z_c compared to other methods. This means that the FR method can support a three-body bound state for a weaker attractive interaction compared to other methods.

Modified FR Method

One can modify the FR method by improving the choice of the variable on which the ground state wavefunction depends. In the simple FR method the distances r_1 and r_2 entered in the definition of the variable R on an equal footing. However, for those configurations of the system in which the two electrons are at unequal distances from the nucleus, the outer electron naturally experiences a smaller effective nuclear charge than the inner one due to shielding. This suggests that r_1 and r_2 cannot be given equal weight in the wavefunction for all values of r_1 and r_2 . So one can define the wavefunction as

$$\psi = \phi(R)$$

$$R = \frac{1}{2}(\alpha r_> + r_< + \eta r_3) \quad , \quad r_1 \neq r_2 \quad (3.23)$$

where $r_> = r_1$ and $r_< = r_2$ for $r_1 > r_2$ and vice-versa. The variable R now contains two variational parameters α and η , one to take into account the screening and the other the interelectronic correlations. Since $R > 0$, the conditions $\alpha + \eta > 0$ and $1 + \eta > 0$ restrict the possible values of α and η . One can note that

$$\alpha r_> + r_< = \frac{\alpha+1}{2} (r_1+r_2) + \frac{\alpha-1}{2} |r_1-r_2| .$$

For the special case of $r_1 = r_2$, one keeps R continuous by defining it as

$$R = \frac{\alpha+1}{2} (r_1+r_2) + \eta r_3$$

which is obvious since when the electrons are equidistant from the nucleus, they must appear in the wavefunction with equal weight.

The Hamiltonian H and the Schrödinger equation in variational form are still given by eqns. (3.15) and (3.16) respectively. One can write

$$\int_0^\infty dr_1 \int_0^\infty dr_2 = \int_0^\infty dr_1 \int_0^{r_1} dr_2 + \int_0^\infty dr_1 \int_{r_1}^\infty dr_2$$

where the first term on the right hand side corresponds to $r_1 > r_2$ and the second term to $r_1 < r_2$. So, for the three possible geometries $r_3 = r_1+r_2$, $r_3 = r_1-r_2$ and $r_3 = r_2-r_1$, one can choose the appropriate forms of the variable R and write eqn (3.16) as

$$\begin{aligned}
0 = \delta \int_0^{\infty} dR \left\{ \frac{2}{\alpha+\eta} \int_0^{2R/(1+\alpha+2\eta)} dR_2 + \frac{2}{1+\eta} \int_{2R/(1+\alpha+2\eta)}^{2R/(\alpha+\eta)} dR_2 \right\} \left\{ X \left(\frac{d\phi}{dR} \right)^2 + E\phi^2 \right. \\
\left. - (v_1+v_2+v_3)\phi^2 \right\} \\
+ \left\{ \frac{2}{\alpha+\eta} \int_0^{2R/(1+\alpha)} dR_2 + \frac{2}{1-\eta} \int_{2R/(1+\alpha)}^{2R/(\alpha+\eta)} dR_2 \right\} \left\{ Y \left(\frac{d\phi}{dR} \right)^2 + E\phi^2 \right. \\
\left. - (v_1+v_2+v_3)\phi^2 \right\} \quad (3.24)
\end{aligned}$$

where

$$\begin{aligned}
X &= -\frac{\hbar^2}{8m} [(\alpha+\eta)^2 + (1+\eta)^2] \\
Y &= -\frac{\hbar^2}{8m} [(\alpha+\eta)^2 + (1-\eta)^2]
\end{aligned}$$

Since ϕ , $\frac{d\phi}{dR}$ and E are independent of R_2 , the corresponding integrals can be easily evaluated and one gets

$$0 = \delta \left[\int_0^{\infty} R dR \left\{ -\frac{\hbar^2}{2M} \left(\frac{d\phi}{dR} \right)^2 - v_{\text{eff}} \phi^2 + E\phi^2 \right\} \right] \quad (3.25)$$

where

$$\frac{1}{M} = \frac{1}{8m(1+\alpha+\eta)} \left[\{(\alpha+\eta)^2 + (1+\eta)^2\} (1+\alpha) + \{(\alpha+\eta)^2 + (1-\eta)^2\} (1+\alpha+2\eta) \right] \quad (3.26)$$

and

$$\begin{aligned}
v_{\text{eff}} &= -\frac{(1+\alpha)(\alpha+\eta)(1+\alpha+2\eta)}{8(1+\alpha+\eta)} \frac{e^2}{R} \\
&\times \left[\frac{1}{\alpha+\eta} \int_0^{2R/(1+\alpha+2\eta)} dR_2 + \frac{1}{1+\eta} \int_{2R/(1+\alpha+2\eta)}^{2R/(\alpha+\eta)} dR_2 + \frac{1}{1-\eta} \int_{2R/(1+\alpha)}^{2R/(\alpha+\eta)} dR_2 \right]
\end{aligned}$$

(continued next page)

$$\begin{aligned}
& + \frac{1}{\alpha+\eta} \int_0^{2R/(1+\alpha)} dR_2 \{ Z\delta(r_1) + Z\delta(r_2) - \delta(r_1-r_2) \} \\
& = - \frac{e^2}{R} \frac{(1+\alpha+2\eta)}{8(1+\alpha+\eta)} [\alpha(2Z-1) + 2Z-\eta] \quad (3.27)
\end{aligned}$$

Using the Euler-Lagrange equation in eqn (3.25) and then substituting $F(R) = R^{1/2}\phi(R)$, one gets the following Schrödinger equation

$$\begin{aligned}
& \left[\frac{\hbar^2}{2m} \left(\frac{d^2 F}{dR^2} + \frac{1}{4R^2} F \right) - \frac{e^2}{R} \frac{[\alpha(2Z-1) + 2Z-\eta](1+\alpha+2\eta)}{2[(\alpha^2+2\eta^2+2\eta\alpha+1)(1+\alpha+\eta)-2\eta^2]} \right] F \\
& = \frac{4(1+\alpha+\eta)}{[(1+\alpha+\eta)(\alpha^2+2\eta^2+2\eta\alpha+1)-2\eta^2]} EF \quad (3.28)
\end{aligned}$$

The solutions of such equations are known analytically. The centrifugal term corresponds to the orbital quantum number $\ell = -\frac{1}{2}$. The ground state energy, in atomic units, is then

$$E_0 = - \frac{(1+\alpha)^2 (1+\alpha+2\eta)^2 \left(Z - \frac{\alpha+\eta}{2(1+\alpha)} \right)^2}{2(1+\alpha+\eta) [(1+\alpha+\eta)(\alpha^2+2\eta^2+2\eta\alpha+1)-2\eta^2]} \quad (3.29)$$

In the special case of $\alpha=1$, eqn (3.29) reduces to eqn (3.21). For a given Z , E_0 in (3.29) is minimised by varying both α and η . Calculated values of E_0 are given in table 1 for different Z . It is seen that the modification in the wavefunction further lowers the ground state energy. One may therefore think of incorporating this improvement in realistic two-electron atomic systems. One can also note that the modi-

fied FR method can support bound helium-like systems at smaller Z_c than the simple FR approximation.



Table 1

Ground state energy^a of one-dimensional helium-like systems with δ -interaction

z	Perturbation [6] $-E_0$	Variational [6] $-E_0$	Hartree-Fock [7] $-E_0$	Kiang [8] $-E_0$	FR ^b		Modified FR ^b		
					η	$-E_0$	α	$-E_0$	$-E_0$
1	0.500	0.563	0.583	0.583	-0.296	0.626	0.712	-0.175	0.640
2	3.000	3.063	3.083	3.107	-0.158	3.136	0.867	-0.108	3.148
3	7.500	7.563	7.583	7.614	-0.108	7.640	0.913	-0.076	7.651
4	14.000	14.063	14.083	14.117	-0.081	14.141	0.935	-0.058	14.152

^aThe energy is given in atomic units.

^bThe optimum values of parameters α and η which minimise E_0 are given.

Table 2 z_c for Helium-like Systems

Perturbation	Variational	Hartree-Fock	FR	Modified FR
1.000	0.854	0.789	0.639	0.511

CHAPTER IV
THE TWO-ELECTRON ATOMIC PROBLEM

The two-electron atomic problem has received considerable attention from the earliest years of quantum mechanics and it still continues to be of current interest. Extensive calculations have been made on helium-like systems, through both variational [1,2] and K-harmonics approach [12-15]. Pekeris [2,11] has determined the upper and lower bounds of the helium atom ground state. His variational calculations for the upper bound were performed with 1078 parameters in the trial wavefunction. On the other hand the K-harmonic approach has attracted attention, but the accuracy of the results is limited by slow convergence and even very involved computations do not yield the desired accuracy.

The FR method was first applied [10] to atomic systems and fairly good results were obtained for the ground state energy of such systems. The authors [10] had hoped that a systematic way to improve the method could be developed. In the last chapter we found that better results could be obtained, in the model one-dimensional problem, by improving the definition of the variable on which the wavefunction depends. Encouraged by this, we attempt here to apply the same modifica-

tion to the realistic two-electron atomic problem.

For simplicity we assume the nucleus to be of infinite mass and stationary at the origin. The Hamiltonian H of the system is

$$H = -\frac{\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2) - ze^2 \left(\frac{1}{x_1} + \frac{1}{x_2} \right) + \frac{e^2}{|x_1 - x_2|} \quad (4.1)$$

where m and $-e$ are respectively mass and charge of an electron and x_1 and x_2 are the electron coordinates.

In terms of the interparticle distances r_1 , r_2 and r_3 , eqn (4.1) reduces to

$$\begin{aligned} H = & -\frac{\hbar^2}{2m} \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + 2 \frac{\partial^2}{\partial r_3^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} + \frac{2}{r_2} \frac{\partial}{\partial r_2} + \frac{4}{r_3} \frac{\partial}{\partial r_3} \right. \\ & + \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \frac{\partial^2}{\partial r_2 \partial r_3} + \frac{r_1^2 + r_3^2 - r_2^2}{r_1 r_3} \frac{\partial^2}{\partial r_1 \partial r_3} \\ & \left. - ze^2 \left(\frac{1}{r_1} + \frac{1}{r_2} \right) + \frac{e^2}{r_3} \right] \quad (4.2) \end{aligned}$$

where $r_1 = |x_1|$, $r_2 = |x_2|$ and $r_3 = |x_1 - x_2|$.

The Schrödinger equation can be obtained by applying the variation $\delta \langle \psi | H | \psi \rangle = 0$, with the restriction that $\langle \psi | \psi \rangle$ is finite. With Hamiltonian in eqn (4.2) this gives

$$\begin{aligned} 0 = & \delta \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_3 r_1 r_2 r_3 \left[\frac{\hbar^2}{2m} \left\{ \left(\frac{\partial \psi}{\partial r_1} \right)^2 + \left(\frac{\partial \psi}{\partial r_2} \right)^2 + 2 \left(\frac{\partial \psi}{\partial r_3} \right)^2 \right. \right. \\ & + \frac{r_2^2 + r_3^2 - r_1^2}{r_1 r_3} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_3} + \frac{r_1^2 + r_3^2 - r_2^2}{r_2 r_3} \frac{\partial \psi}{\partial r_2} \frac{\partial \psi}{\partial r_3} \left. \right\} \\ & \left. + \left\{ \frac{e^2}{r_3} - ze \left(\frac{1}{r_1} + \frac{1}{r_2} \right) - E \right\} \psi^2 \right] \quad (4.3) \end{aligned}$$

In ref. [10], the wavefunction ψ was defined by assuming it to be dependent on a single non-negative variable

$$R = \frac{1}{2}(r_1 + r_2 + \eta r_3)$$

where η is a variational parameter. However, we have seen that the value for the ground state energy of one-dimensional helium-like model is significantly improved by modifying the definition of the variable R . So we try out the same modification in helium-like atomic systems. Defining

$$\psi = \phi(R)$$

$$R = \frac{1}{2}(\alpha r_{>} + r_{<} + \eta r_3)$$

where $r_{>} = r_1$ and $r_{<} = r_2$ for $r_1 > r_2$ and vice-versa. α and η are the two variational parameters. We now choose the variables R , $R_2 = r_2$ and $R_3 = r_3$, so that R is an independent variable.

To perform integration in eqn (4.3), the region $r_1 > r_2$ need only be considered as ϕ and the various terms in eqn (4.3) are symmetric in r_1 and r_2 . Changing the variable gives

$$dr_1 dr_2 dr_3 = \frac{2}{\alpha} dR dR_2 dR_3$$

Referring to Fig. 1a, one notes that for a given R defined for $r_1 > r_2$, the region of integration is the plane HIJ. However, the triangular conditions $r_1 + r_2 > r_3$, $r_2 + r_3 > r_1$ and $r_3 + r_1 > r_2$ restrict the region of integration to the plane LMN. A plane intersecting the plane LMN along the line LQ where Q

is the mid point of line MN, divides the plane LMN into two regions; plane LQN corresponding to $r_1 > r_2$ and plane LMQ corresponding to $r_1 < r_2$. To integrate over the variables R_2 and R_3 first, for $r_1 > r_2$, one obtains the required plane of integration ABC by projecting the plane NQL on the R_2 - R_3 plane as depicted in Fig. 1b. Since the wavefunction ϕ depends only on R , integration in eqn (4.3) over other variables R_2 and R_3 can be performed.

Denoting half of the volume integral by $\int [dr]$, we have

$$\begin{aligned}
 \int [dr] &= \int_0^\infty dr_1 \int_0^{r_1} dr_2 \int_{r_1-r_2}^{r_1+r_2} dr_3 r_1 r_2 r_3 \\
 &= \frac{2}{\alpha} \int_0^\infty dR \left[\int_0^{2R/(1+\alpha+2\eta)} dR_2 \int_{\frac{1}{\alpha+\eta}(2R-(1-\alpha)R_2)}^{\frac{1}{\alpha+\eta}(2R-(1-\alpha)R_2)} dR_3 \right. \\
 &\quad \left. + \int_{2R/(1+\alpha+2\eta)}^{2R/(1+\alpha)} dR_2 \int_{\frac{1}{\alpha+\eta}(2R-(1+\alpha)R_2)}^{\frac{1}{\eta}(2R-(1+\alpha)R_2)} dR_3 \right] R_2 R_3 (2R-R_2-\eta R_3) \\
 &= p \int_0^\infty R^5 dR \tag{4.4}
 \end{aligned}$$

where

$$\begin{aligned}
p = \frac{2^6}{15} & [2(1+\alpha+\eta)^2 \{2-(1+\alpha+\eta)(1-5\alpha-4\eta)\} \\
& + \eta(1+\alpha)(1+\alpha+2\eta) - 3(\alpha+\eta)(1+\alpha)^2 \\
& - (1+\alpha)^2] / [(1+\alpha)^3 (\alpha+\eta)^3 (1+\alpha+2\eta)^4] \quad (4.5)
\end{aligned}$$

Similarly, one can show, after lengthy but straightforward manipulation that

$$\int [dr] \left\{ \alpha \frac{r_1^2 + r_3^2 - r_2^2}{r_1 r_3} + \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \right\} = q \int_0^\infty R^5 dR \quad (4.6)$$

$$\int [dr] \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = s \int_0^\infty R^4 dR \quad (4.7)$$

$$\int [dr] \frac{1}{r_3} = t \int_0^\infty R^4 dR \quad (4.8)$$

where

$$\begin{aligned}
q = \frac{2^8}{15} & [2(1+\alpha+\eta)^3 \{2(1+\alpha+\alpha^2) - \eta(1-\alpha)\} \\
& - 2(1+\alpha)(1+\alpha+\eta)(1+\alpha+2\eta+\eta^2) \\
& - (1+\alpha)^3 (2+3\alpha+4\eta)] / [(1+\alpha)^3 (\alpha+\eta)^3 (1+\alpha+2\eta)^4] \quad (4.9)
\end{aligned}$$

$$\begin{aligned}
s = \frac{2^4}{3} & [2(1+\alpha+\eta)^2 \{5(\alpha+\eta)-1\} - 2\eta^3 + \eta(1-\alpha)^2 \\
& + 3(1-\alpha^2)] / [(1+\alpha)^2 (\alpha+\eta)^3 (1+\alpha+2\eta)^3] \quad (4.10)
\end{aligned}$$

$$\begin{aligned}
t = \frac{2^4}{3} & [4(\alpha+\eta)(1+\alpha+\eta)^2 + (1+\alpha)(1+\alpha+2\eta)] / \\
& [(1+\alpha)^3 (\alpha+\eta)^2 (1+\alpha+2\eta)^3] \quad (4.11)
\end{aligned}$$

Using these relations, eqn (4.3) reduces to

$$0 = \delta \int_0^{\infty} R^5 dR \left[-\frac{\hbar^2}{2m} \left(\frac{d\phi}{dR} \right)^2 \left\{ \frac{(1+\alpha^2+2\eta^2)}{4} p + \frac{\eta}{4} q \right\} + \frac{e^2}{R} (Zs-t) \phi^2 + pE\phi^2 \right] . \quad (4.12)$$

Using the Euler-Lagrange equation one gets a Schrödinger like equation

$$-\frac{\hbar^2}{2m} \left[\frac{(1+\alpha^2+2\eta^2)}{4} p + \frac{\eta}{4} q \right] \frac{1}{R^5} \frac{d}{dR} \left(R^5 \frac{d\phi}{dR} \right) - \frac{e^2}{R} (Zs-t) \phi = pE\phi. \quad (4.13)$$

On making the substitution $F(R) = R^{5/2} \phi(R)$, eqn (4.13) leads to the following differential equation

$$\frac{\hbar^2}{2m} \left[\frac{(1+\alpha^2+2\eta^2)}{4} p + \frac{\eta}{4} q \right] \left(-\frac{d^2 F}{dR^2} + \frac{15}{4R^2} F \right) - \frac{e^2}{R} (Zs-t) F = pEF. \quad (4.14)$$

This is the wave equation of a particle in a coulomb potential with effective orbital momentum number $\ell = \frac{3}{2}$. The solutions of such equations are known analytically. For the special case of $\alpha = 1$, eqn (4.14) reduces to eqn. (6) of ref. [10]. The ground state energy E_0 , in atomic units, corresponding to the principle quantum number $n = \frac{5}{2}$ is

$$E_0 = -\frac{2}{\left(\frac{5}{2}\right)^2} \frac{(Zs-t)^2}{p\{(1+\alpha^2+2\eta^2)p+\eta q\}} \quad (4.15)$$

and the unnormalized ground state wavefunction ϕ_0 is

$$\phi_0 = R^{-5/2} F_0(R) = \exp\left[-\frac{R}{a} \frac{8(Zs-t)}{5\{(1+\alpha^2+2n^2)p+\eta q\}}\right]. \quad (4.16)$$

For a given Z , E_0 is minimised with respect to the parameters α and η . The calculated values of E_0 for different Z are given in table 3 and are compared with the results of ref [10] and the best estimates of Pekeris [2]. The values of E_0 from different methods given in the table have been calculated with the assumption that the nucleus is infinitely heavy. However, the finite mass of the nucleus can be easily taken into account in the FR formalism. Our results are consistently better than the conventional one parameter variational calculations [16] and the simple FR approximation [10].

From table 3 we can see that except in the case of H^- , the best estimate for E_0 is lower than our result by about 0.005 a.u. only while for H^- this difference is 0.007. Although the FR method has the merit of yielding simple analytic expressions for the energy and the wavefunction of the two-electron atomic systems, it cannot compete in accuracy with the more elaborate variational calculations.

By an inspection of the wavefunction $\phi_0(R)$ in eqn (4.16), one can say that by choosing at the outset a wavefunction of the form

$$\phi_0 = e^{-\lambda R}$$

where λ is a variational parameter, the ground state energy

of the system could be determined as well. However, in the framework of FR formalism, we show that if the wavefunction is a function of the single non-negative variable R , the best form of ϕ_0 is exponential in nature. The inclusion of the interelectronic distance r_3 in the exponent may be an efficient way of taking interelectronic correlations into account.

We now compare the FR approach with the K-harmonics approach. One knows that if only the $K=0$ component is retained in the wavefunction, the problem reduces to solving a single differential equation in the variable $\rho = (r_1^2 + r_2^2 + r_3^2)^{1/2}$, instead of R in the FR formalism. This differential equation was first solved by Morpurgo [17] for a model triton problem. McMillan [18] using different forms of nuclear potentials has shown that the FR approximation yields better results than the Morpurgo equation in the case of triton. The Morpurgo equation, however, has the advantage that it can be systematically developed through the K-harmonics approach.

In the K-harmonic formalism, where an infinite set of coupled differential equations of a single variable is obtained, one has to truncate the set at some point and solve the coupled equations numerically to estimate the energy eigenvalues of the three-body system. It has been shown [15] in the case of helium atom that rapid convergence of the K-harmonic expansion does not occur and hence a large number of coupled equations are necessary to achieve good accuracy in the ground

state energy. Darling and Schoucri [15] have made calculations up to 16 terms and they quote the value -0.28871 a.u. for the ground state energy, which is about 0.011 a.u. higher than our estimate. Whitten and Sims [12] carried out calculations up to 8 terms, obtaining a value -2.8443 a.u. for helium atom ground state energy. However, they improved their results by incorporating the variational approach in K-harmonics by introducing a few variational parameters in the K-harmonic wavefunction. The value for the helium atom ground state energy was -2.90107 a.u., which is slightly better than our present estimate.

Summarizing, we note that the FR method yields simple analytic solutions with minimum computational work involved. Even then, the results are comparable in accuracy with the results obtained from the more elaborate K-harmonics approach. However the FR approximation in its present form cannot compete in accuracy with the conventional variational calculations involving many variational parameters.

Table 3
Ground state energy^a of helium-like atoms

Two electron system	Previous ^b calculation $-E_0$	Present Calculation ^c			Best Estimate ^d $-E_0$
		α	η	$-E_0$	
H ⁻	0.5079	0.6894	-0.1735	0.5206	0.5278
He	2.8896	0.8931	-0.1102	2.8983	2.9037
Li ⁺	7.2668	0.9340	-0.0767	7.2748	7.2799
Be ⁺⁺	13.6429	0.9522	-0.0587	13.6505	13.6556

^aThe energy is given in atomic units.

^bRef. [10].

^cThe optimum values of α and η which minimise E_0 of eqn (4.15).

^dRef. [2].

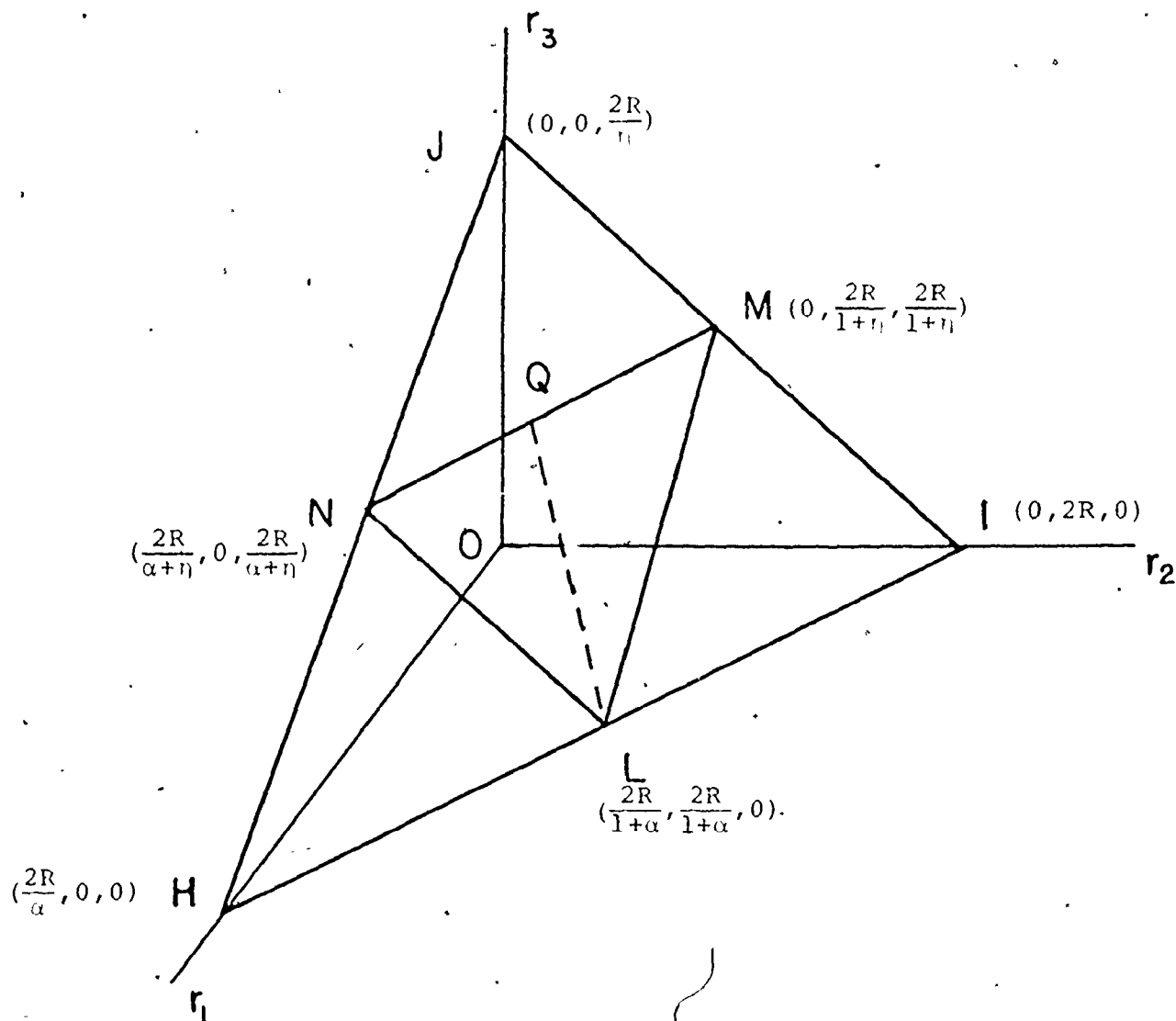


Fig. 1a. The plane of integration for a given R is the plane HIJ . The triangular conditions $r_1+r_2 > r_3$ etc. restrict the region of integration to the plane NML . A plane intersecting the plane NQL along the line LQ where Q is the mid-point of line NM , divides the plane into two parts; plane NQL corresponding to $r_1 > r_2$ and plane LMQ corresponding to $r_1 < r_2$.

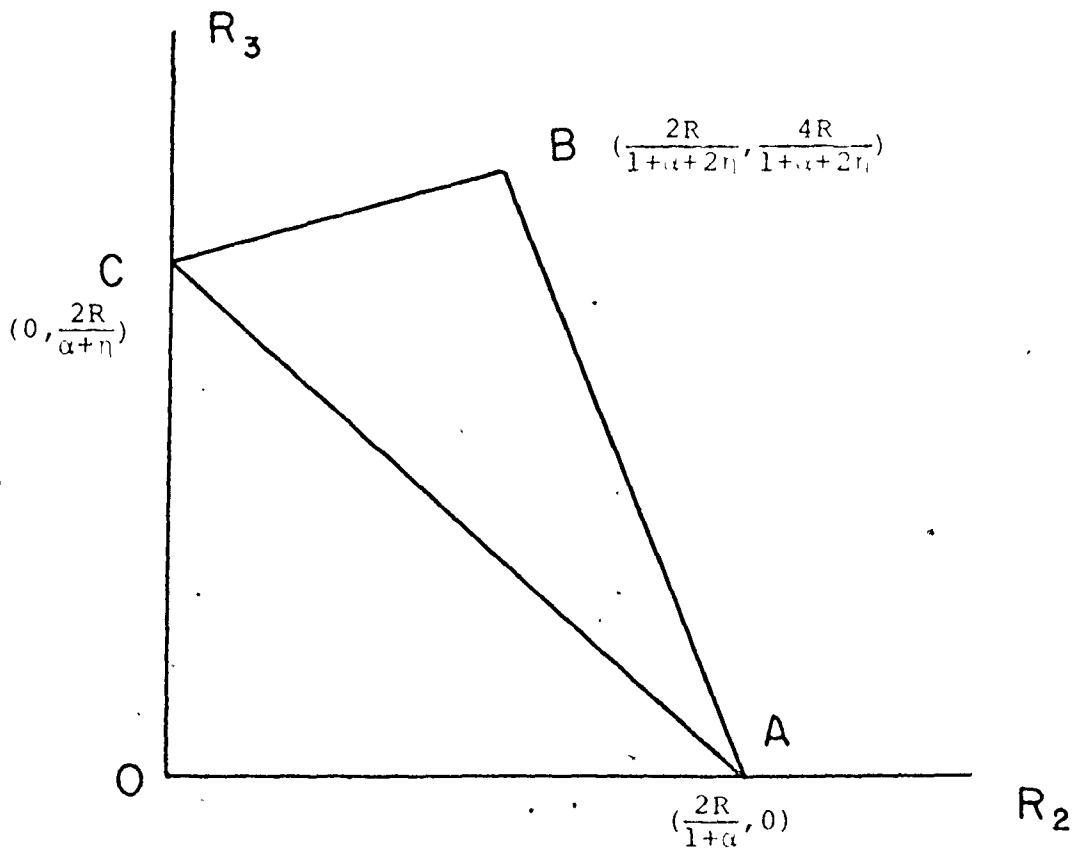


Fig. 1b. The region of R_2 - R_3 integration for r_1, r_2 is the plane ABC which is the projection of the plane NQL (fig. 1a) on the R_2 - R_3 plane.

APPENDIX

We give here some of the mathematical details for the derivation of eqns (2.11), (2.14), (2.15) and (2.16) in Chapter II for the generalised FR approximation in three dimensions [4].

The Hamiltonian H in relative coordinates for a three body system interacting via central forces is

$$\begin{aligned}
 H = \sum_{\text{cyclic}} & \left[-\frac{\hbar^2}{2} \left\{ \left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1} \frac{\partial}{\partial r_1} \right) \right. \right. \\
 & \left. \left. + \frac{1}{m_1} \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \frac{\partial^2}{\partial r_2 \partial r_3} \right\} + v_1(r_1) \right] \quad (\text{A-1})
 \end{aligned}$$

where m_1 is the mass of particle 1 and r_1 is the distance between particles 2 and 3 and so on. The variational principle for the Schrödinger equation may then be written as

$$\begin{aligned}
 0 = \delta \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_3 r_1 r_2 r_3 \\
 \times \left[-\frac{\hbar^2}{2} \left\{ \left(\frac{1}{m_2} + \frac{1}{m_3} \right) \left(\frac{\partial \psi}{\partial r_1} \right)^2 + \left(\frac{1}{m_3} + \frac{1}{m_1} \right) \left(\frac{\partial \psi}{\partial r_2} \right)^2 + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \left(\frac{\partial \psi}{\partial r_3} \right)^2 \right. \right.
 \end{aligned}$$

(equation continued next page)

$$\begin{aligned}
& + \frac{1}{m_1} \frac{r_2^2 + r_3^2 - r_1^2}{r_2 r_3} \left\{ \frac{\partial \psi}{\partial r_2} \frac{\partial \psi}{\partial r_3} + \frac{1}{m_2} \frac{r_3^2 + r_1^2 - r_2^2}{r_1 r_3} \frac{\partial \psi}{\partial r_3} \frac{\partial \psi}{\partial r_1} \right. \\
& \left. + \frac{1}{m_3} \frac{r_1^2 + r_2^2 - r_3^2}{r_1 r_2} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_2} \right\} - \{v_1(r_1) + v_2(r_2) + v_3(r_3)\} \psi^2 + E \psi^2 \}. \quad (\text{A-2})
\end{aligned}$$

The three-body wavefunction ψ , assumed to be spherically symmetric, is defined as

$$\psi = \phi(R)$$

$$R = \frac{1}{2}(\eta_1 r_1 + \eta_2 r_2 + \eta_3 r_3) \quad (\text{A-3})$$

where η 's are variational parameters.

The transformation of variables from the old set (r_1, r_2, r_3) to the new set (R, R_2, R_3) where $R_2 = r_2$ and $R_3 = r_3$ is given by

$$dR dR_2 dR_3 = \frac{\partial(R)}{\partial(r)} dr_1 dr_2 dr_3,$$

where the Jacobian

$$\frac{\partial(R)}{\partial(r)} = \begin{vmatrix} \frac{\partial R}{\partial r_1} & \frac{\partial R}{\partial r_2} & \frac{\partial R}{\partial r_3} \\ \frac{\partial R_2}{\partial r_1} & \frac{\partial R_2}{\partial r_2} & \frac{\partial R_2}{\partial r_3} \\ \frac{\partial R_3}{\partial r_1} & \frac{\partial R_3}{\partial r_2} & \frac{\partial R_3}{\partial r_3} \end{vmatrix}$$

$$= \frac{1}{2} \eta_1$$

so that

$$dr_1 dr_2 dr_3 = \frac{2}{\eta_1} dR dR_2 dR_3.$$

One must now find the limits of R , R_2 and R_3 . Consider Fig. 2a. For a given R , the definition of R in (A-3) represents a plane PQR with intercepts $2R/\eta_1$, $2R/\eta_2$ and $2R/\eta_3$ respectively. However, the triangular conditions $r_1+r_2+r_3$ etc. restrict the region of integration to the plane LMC. To perform R_2 and R_3 integrations first, one considers the plane ABC in Fig. 2b which is the projection of plane LMC on the R_2 - R_3 plane. Thus the volume integral can be written as

$$\begin{aligned}
 \int (dr) r_1 r_2 r_3 &= \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1-r_2|}^{r_1+r_2} dr_3 r_1 r_2 r_3 \\
 &= \frac{2}{\eta_1} \int_0^\infty dR \left[\int_0^{2R/(\eta_1+\eta_2)} dR_2 \int_{\frac{2R-(\eta_1+\eta_2)R_2}{\eta_3+\eta_1}}^{\frac{2R+(\eta_1-\eta_2)R_2}{\eta_3+\eta_1}} dR_3 \right. \\
 &\quad \left. + \int_{2R/(\eta_1+\eta_2)}^{2R/(\eta_2+\eta_3)} dR_2 \int_{\frac{2R-(\eta_1+\eta_2)R_2}{\eta_3-\eta_1}}^{\frac{2R+(\eta_1-\eta_2)R_2}{\eta_3+\eta_1}} dR_3 \right] (2R-\eta_2 R_2 - \eta_3 R_3) R_2 R_3 \\
 &\qquad\qquad\qquad (A-4)
 \end{aligned}$$

While depicting the region of integration in Fig. 2a, it has been assumed that $\eta_1 > \eta_2 > \eta_3$. However, the final results are independent of such assumptions. With the help of eqn (A-4) one finds

$$\int (dr) r_1 r_2 r_3 = 2\xi \int_0^\infty R^5 dR \quad (\text{A-5})$$

$$\int (dr) r_1 (r_2^2 + r_3^2 - r_1^2) = 2\eta_1 \xi \int_0^\infty R^5 dR \quad (\text{A-6})$$

where explicit forms for ξ and η_1 are given in eqns (2.14) and (2.15) respectively of chapter II.

The integrations over the two-body potentials are not straightforward. For instance, integration over R_3 cannot be performed in the following integral

$$\int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_3 r_1 r_2 r_3 v_1(r_1) \quad (\text{A-7})$$

since by definition $r_1 = (2R - r_2 R_2 - \eta_3 R_3) / \eta_1$. We therefore use the cyclic permutation of r_1 , r_2 and r_3 which leaves the volume integral unchanged to write the above integral as

$$\int_0^\infty dr_3 \int_0^\infty dr_1 \int_{|r_3 - r_1|}^{r_3 + r_1} dr_2 r_1 r_2 r_3 v_1(r_1). \quad (\text{A-8})$$

Accordingly, the definition of the new variables is

$$R_3 = \frac{1}{2}(\eta_1 r_1 + \eta_2 r_2 + \eta_3 r_3)$$

$$R = r_1$$

$$R_2 = r_2$$

so that integral (A-8) becomes

$$= \frac{2}{\eta_3} \int_0^\infty dR_3 \int_0^{R_3} dR \int dR_2 (2R_3 - \eta_1 R - \eta_2 R_2) R R_2 v_1(R) \quad (4-9)$$

Integration over R_2 can now be performed by defining the region of integration in the R - R_2 plane. Integral (A-9) is then

$$= \frac{2}{\eta_3} \int_0^\infty dR_3 \left[\int_0^{2R_3/(\eta_1+\eta_3)} dR \int_{\frac{(2R_3 - (\eta_1+\eta_3)R)}{\eta_2+\eta_3}}^{\frac{(2R_3 + (\eta_3 - \eta_1)R)}{\eta_2+\eta_3}} dR_2 \right. \\ \left. + \int_{2R_3/(\eta_1+\eta_3)}^{2R_3/(\eta_1+\eta_2)} dR \int_{\frac{(2R_3 - (\eta_1+\eta_3)R)}{\eta_2 - \eta_3}}^{\frac{(2R_3 + (\eta_3 - \eta_1)R)}{\eta_2+\eta_3}} dR_2 \right] (2R_3 - \eta_1 R - \eta_2 R_2) R_2 R v_1(R) \quad (A-10)$$

After performing the R_2 integration, one gets

$$\int (dr) r_1 r_2 r_3 v_1(r_1) = \int_0^\infty R^5 W_1(R) dR \quad (A-11)$$

where $W_1(R)$ has been defined in eqn (2.16) of chapter II.

Similarly one can make cyclic permutation of variables to evaluate the integrals containing $v_2(r_2)$ and $v_3(r_3)$.

Eqn (A-2) can now be written as

$$0 = \delta \int_0^\infty R^5 dR \left[-\frac{\hbar^2}{4} \left\{ \xi \left[\frac{1}{m_2} + \frac{1}{m_3} \right] \eta_1^2 + \left(\frac{1}{m_3} + \frac{1}{m_1} \right) \eta_2^2 + \left(\frac{1}{m_1} + \frac{1}{m_2} \right) \eta_3^2 \right\} \right. \\ \left. + \zeta \eta_1 \eta_2 \eta_3 \left(\frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3} \right) \right] \left(\frac{d\phi}{dR} \right)^2 - (W_1(R) + W_2(R) + W_3(R)) \phi^2 + 2\xi E \phi \quad (A-12)$$

Defining reduced mass m by eqn (2.12), one has

$$0 = \delta \int_0^{\infty} R^5 dR \left[-\frac{\hbar^2}{m} \left(\frac{d\phi}{dR} \right)^2 + 8\xi E \phi^2 - 4(W_1 + W_2 + W_3) \phi^2 \right] . \quad (\text{A-12})$$

Using Euler-Lagrange equation, one gets

$$-\frac{\hbar^2}{m} \frac{1}{R^5} \frac{d}{dR} \left(R^5 \frac{d\phi}{dR} \right) - 8\xi E \phi + 4(W_1 + W_2 + W_3) \phi = 0 . \quad (\text{A-13})$$

Substituting $F(R) = R^{5/2} \phi(R)$ in the above equation, the differential equation obtained is

$$-\frac{\hbar^2}{m} \frac{d^2 F}{dR^2} + V(R)F = 8\xi EF \quad (\text{A-14})$$

where $V(R)$ is defined in eqn (2.13). The Schrödinger equation (A-14) is eqn (2.11) of chapter II.

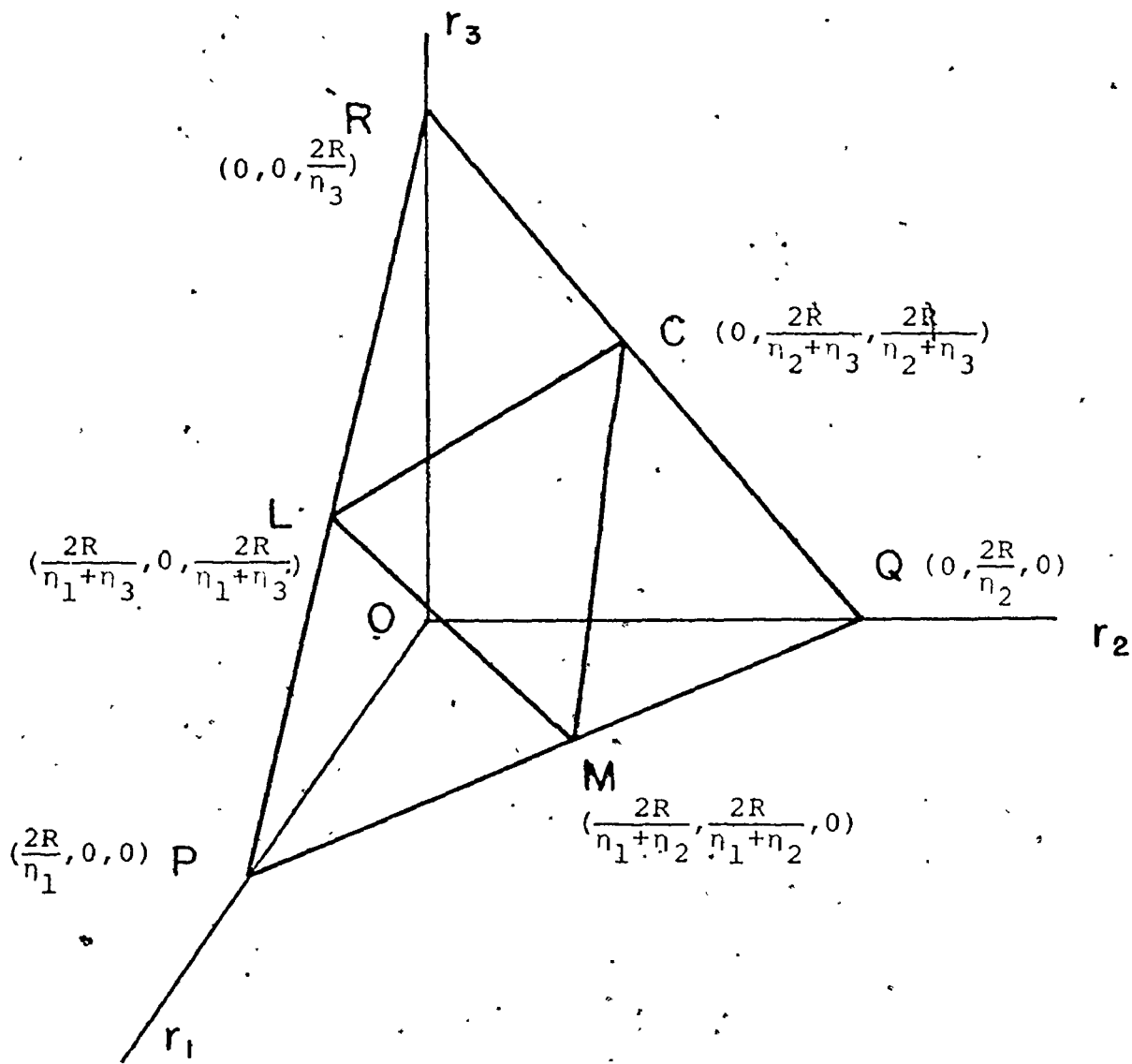


Fig. 2a. The plane of integration for a given R is the plane PQR . The triangular conditions $r_1 + r_2 > r_3$ etc. limit the region of integration to the plane LCM .

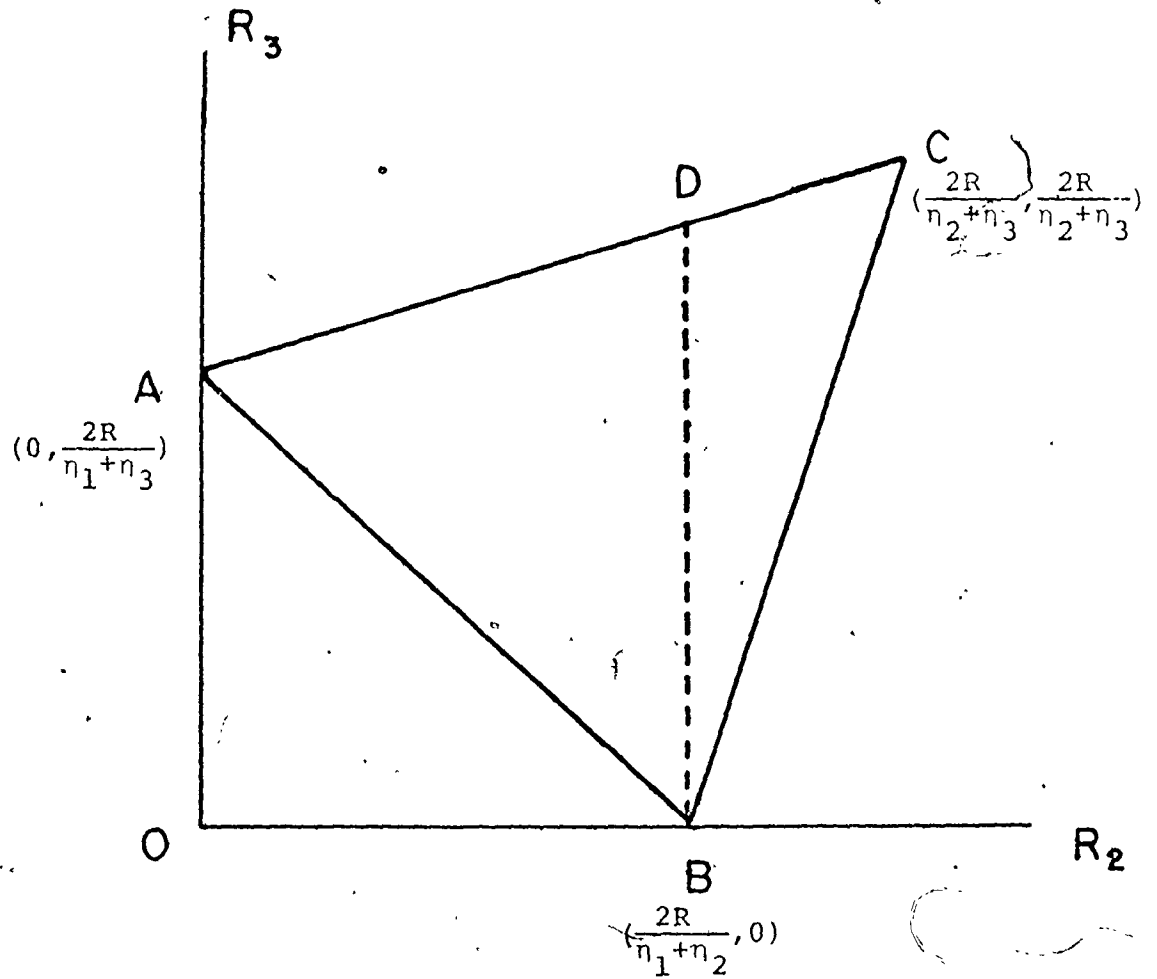


Fig. 2b. The projection of the plane LCM (fig. 2a) on the R_2 - R_3 plane is ACB which is the region for R_2 - R_3 integration.

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