

New Method for Calculating Molecular Orbitals with Application to Cyclic Systems

LEONARD EYGES

Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts*

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We consider the molecular orbital problem, i.e., the quantum-mechanical problem of a particle (electron) bound to a configuration of N potentials, when the potentials may overlap. We show why, when the individual potentials are spherically symmetric, it is advantageous to write the wave function Ψ in the many-center (LCAO) form, $\Psi = \psi^{(1)}(\mathbf{r}_1) + \dots + \psi^{(N)}(\mathbf{r}_N)$, where \mathbf{r}_i refers to a coordinate system associated with the i th potential. The main point of this paper is to show that it is not only advantageous to use this form, but that it is also practical to directly determine the "atomic orbitals" $\psi^{(1)} \dots \psi^{(N)}$. To show this we define the $\psi^{(i)}(\mathbf{r}_i)$ in a natural way and then use the Schrödinger equation to get a set of coupled integral equations for these functions and to get an analogous set for $\phi^{(i)}(\mathbf{r}_i)$, their Fourier transforms. We expand the $\phi^{(i)}(\mathbf{r}_i)$ in partial waves and make it plausible that the resultant sets of equations can be truncated and that frequently only a small number of partial waves need be retained, so that the equations are practical to solve.

To show the spirit of the method we discuss, as a simple application, the ground state of cyclic systems, i.e., of potentials arranged at the vertices of regular polygons. The truncation of the equations then gives an approximate equation for the "S-wave part" of the orbitals and an expression which enables us to estimate the higher order partial waves from this S-wave part. We present methods for approximately solving the S-wave equation, which equation

has the advantage of strongly resembling the corresponding one for a single potential, except for a "structure factor" which depends on the configuration. These methods include a variational method which does not involve multicenter integrals, a means of reducing the problem to that of solving the Schrödinger equation for an effective potential, and a method involving screened nuclear charge. For Coulomb potentials and for $N=2,3,4$ ($N=2$ corresponding to the hydrogen molecule ion) we calculate the S-wave part of the orbitals using the latter method; in these calculations arbitrary N is not essentially more difficult than $N=2$.

As a further application we use the second of the equations mentioned above to calculate, for $N=2$, the P-wave or "polarization" terms in the orbitals. We get good agreement for the form of this part of the wave function with the best variational calculation of this kind, that of Dickinson.

Finally, we point out that these two applications are the first steps in an iterative procedure which seems to be promising more generally. Namely, starting from an approximation to an orbital which involves, say, one or more dominant partial waves, it would now appear that one can both calculate the other partial-wave components and correct the initial approximation, and so by iteration arrive at the correct form of the orbital.

I. INTRODUCTION

IN a previous paper¹ we have considered the quantum-mechanical problem of a single particle (electron) bound to more than one attractive potential, with the important restriction that the potentials have finite range, and are arranged in such a configuration that they do not overlap. A problem which is at least equally as important, e.g., in the theory of molecules, is the more general one in which the potentials overlap, as they necessarily do if they are of infinite range, and possibly do if they are of finite range. It is this problem of overlapping potentials that we discuss in the present paper.

In this kind of multicenter problem the first question that faces one is that of choice of a coordinate system. Should one express the wave function in terms of a single coordinate system, with origin chosen as conveniently as possible? Or should one set up more than one coordinate system and try to write the wave function as a sum of functions each referring to one of the different systems? For nonoverlapping potentials, we saw that the latter procedure was advantageous.¹ One could easily set up the formal solution if one used a set of coordinate systems, one for each potential. And, of course, this multicenter representation is what one tries in the LCAO (linear combination of atomic

orbitals) method of dealing with many-centered potentials.

These facts aside there is, it seems to us, a more important reason for preferring, or at least for investigating thoroughly, a multicenter representation. It is the question of obtaining the best convergence of the solution, or more specifically the best convergence of the partial-wave expansions one ordinarily uses. We can illustrate this point simply by considering a particle bound to two identical potentials, say a distance d apart. We consider the convergence properties of the solution expressed in a two-center representation, one coordinate system centered at each potential, and in a one-center representation with, say, a coordinate system midway between the potentials. Now, for $d \rightarrow 0$ there is no difference in the convergence properties of the one and two-center representations, since they coincide. For d very large, however, the ground-state wave function of the system will be a linear combination in the two-center representation of an S state in the first coordinates plus an S state in the second coordinates. If, however, we imagine this wave function expanded in terms of spherical harmonics of the one-center representation, it is clear that the convergence of the expansion would be very poor; many terms would be needed to represent what are simple S states in two-center coordinates. For intermediate distances it is plausible that the convergence will remain better in a multicenter representation.

We can see somewhat more generally why we would

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¹ L. Eyges, Phys. Rev. **111**, 683 (1958).

expect better convergence with a multicenter representation of the wave function. To do this we imagine N spherically symmetric potentials whose centers are at $\mathbf{d}_1 \cdots \mathbf{d}_N$ with respect to some general coordinate system. We suppose that there is, in addition, a spherical coordinate system, whose orientation we leave arbitrary for the moment, at the center of each potential. Let \mathbf{P} be a vector in the general system to a point in space and let \mathbf{r}_i be the vector in the i th coordinate system to the same point in space. Then for the potentials i and n we have $\mathbf{r}_i + \mathbf{d}_i = \mathbf{r}_n + \mathbf{d}_n$ or

$$\mathbf{r}_i = \mathbf{r}_n + \mathbf{d}_{in}, \quad (1)$$

where

$$-\mathbf{d}_{in} = \mathbf{d}_i - \mathbf{d}_n. \quad (2)$$

The wave function Ψ is a function of \mathbf{P} and satisfies the integral equation

$$\Psi(\mathbf{P}) = - \int \Psi(\mathbf{P}') v(\mathbf{P}') g_\beta(\mathbf{P}, \mathbf{P}') d\mathbf{P}', \quad (3)$$

where $V(\mathbf{P}')$ is the potential at \mathbf{P}' , $\beta^2 = 2m|E|/\hbar^2$ for a bound state, E is an energy eigenvalue, and $v(\mathbf{P}) = (2m/\hbar^2)V(\mathbf{P})$. Here $g_\beta(\mathbf{P}, \mathbf{P}')$ is a Green's function which has the form

$$g_\beta(\mathbf{P}, \mathbf{P}') = \exp(-\beta|\mathbf{P} - \mathbf{P}'|)/4\pi|\mathbf{P} - \mathbf{P}'|. \quad (4)$$

It satisfies the differential equation

$$(\nabla^2 - \beta^2)g_\beta = -\delta(\mathbf{P} - \mathbf{P}'), \quad (5)$$

where $\delta(\mathbf{P})$ is a three-dimensional delta function. This last equation can be used with the integral equation (3) to prove that that equation is equivalent to the Schrödinger differential equation

$$(\nabla^2 - \beta^2)\Psi(\mathbf{P}) = v(\mathbf{P})\Psi(\mathbf{P}). \quad (6)$$

Finally, $v(\mathbf{P})$ for the multicentered potential we discuss is of the form

$$v(\mathbf{P}) = v_1(\mathbf{r}_1) + \cdots + v_N(\mathbf{r}_N). \quad (7)$$

Now we return to the discussion of the convergence properties of the solution for this multicentered potential. Let us suppose for a moment that we knew the wave function $\Psi(\mathbf{P})$, not necessarily in an analytic form; for example, we might be given the wave function in the form of a table, one entry for each point of space. We can imagine that we then used this tabular wave function to evaluate the integral in Eq. (3) and so get an analytic expression for Ψ . Now the Green's function is a function only of the difference between \mathbf{P} and \mathbf{P}' and in using it we can express it in any coordinate system we wish. For example, we can equally well use any of the N representations, for $i=1, \cdots, N$

$$g_\beta = \exp(-\beta|\mathbf{r}_i - \mathbf{r}_i'|)/4\pi(|\mathbf{r}_i - \mathbf{r}_i'|). \quad (8)$$

With this in mind, we put the expression (7) for the potential energy into Eq. (3). We get, in a somewhat

mixed, but, we trust, clear notation

$$\Psi(\mathbf{P}) = - \int \Psi(\mathbf{P}') [v_1(\mathbf{r}_1') + \cdots + v_N(\mathbf{r}_N')] g_\beta(\mathbf{P}, \mathbf{P}') d\mathbf{P}'. \quad (9)$$

Now let us consider the i th integral in the last expression, i.e., the integral over $v_i(\mathbf{r}_i')$. In this integral we can express the Green's function in $\mathbf{r}_i, \mathbf{r}_i'$ coordinates and the integration then gives rise to a function $\psi^{(i)}(\mathbf{r}_i)$

$$\psi^{(i)}(\mathbf{r}_i) = - \int \Psi(\mathbf{P}') v_i(\mathbf{r}_i') g_\beta(\mathbf{r}_i, \mathbf{r}_i') d\mathbf{r}_i', \quad (10)$$

and Eq. (9) becomes

$$\Psi(\mathbf{P}) = \psi^{(1)}(\mathbf{r}_1) + \cdots + \psi^{(N)}(\mathbf{r}_N). \quad (11)$$

We consider the integral over $d\mathbf{r}_i'$ in Eq. (10) as an integral over the solid angle Ω_i' times an integral over the magnitude of \mathbf{r}_i' , i.e., $d\mathbf{r}_i' \rightarrow r_i'^2 dr_i' d\Omega_i'$. Now in evaluating the integral over the solid angle $d\Omega_i'$ we must imagine $\Psi(\mathbf{P}')$ expressed in spherical harmonics of Ω_i' and can imagine g_β (as a function of $\mathbf{r}_i, \mathbf{r}_i'$) also expressed in spherical harmonics of Ω_i' . We then have under the integral sign a series of products of *two* spherical harmonics of Ω_i' and the convergence of the expansion for $\psi^{(i)}(\mathbf{r}_i)$ as a function of Ω_i' will be better, the better the convergence of this double series. We have a product of two and not three spherical harmonics to integrate over because in the i th coordinate system (and only in the i th system) $v_i(\mathbf{r}_i)$ has a trivial expansion in spherical harmonics. The point we are trying to make is that in this way of evaluating the wave function we take maximum advantage of the fact that $v_i(\mathbf{r}_i)$ is spherically symmetric. By contrast, imagine that we had simply used Eq. (3) to evaluate the wave functions as a function of \mathbf{P} , in some coordinate system which has no special relation to the i th potential. Then in doing the integration we must imagine $\Psi(\mathbf{P}')$ expanded in spherical harmonics of $\Omega_{P'}$, similarly for g_β as a function of \mathbf{P}' and must imagine that $v_i(\mathbf{r}_i)$ is also expressed in a series of spherical harmonics of $\Omega_{P'}$. Thus, we have to integrate *three* spherical harmonics and this will lead, in general, to an expansion of $\Psi(\mathbf{P})$ in spherical harmonics of Ω_P which converges poorly, especially if the potential v_i is far from the origin.

To state in a nutshell the advantage of dealing with the representation (11): It is the way of expressing the wave function that takes full advantage of the fact that the individual potentials are spherically symmetric. Conversely, if the individual potentials are not spherically symmetric (or almost so), there is no point to using a representation like (11).

II. THE GENERAL MULTICENTER EQUATIONS

For the reasons given above we wish to use a multicenter representation for the wave function, of the form of Eq. (11). How can we determine the $\psi^{(i)}(\mathbf{r}_i)$? The

answer is given by Eqs. (10) and (11). We simply consider these equations as a set of integral equations which must be solved. More explicitly, let us write out Eq. (10) for $i=1\cdots N$ and put in on the right-hand side of each of these equations the expression (11) for $\Psi(\mathbf{P}')$. We get

$$\begin{aligned}\psi^{(1)}(\mathbf{r}_1) &= - \int [\psi^{(1)}(\mathbf{r}_1') + \cdots \psi^{(N)}(\mathbf{r}_N')] \\ &\quad \times v_1(\mathbf{r}_1') g_\beta(\mathbf{r}_1, \mathbf{r}_1') d\mathbf{r}_1', \\ \vdots \\ \psi^{(N)}(\mathbf{r}_N) &= - \int [\psi^{(1)}(\mathbf{r}_1') + \cdots \psi^{(N)}(\mathbf{r}_N')] \\ &\quad \times v_N(\mathbf{r}_N') g_\beta(\mathbf{r}_N, \mathbf{r}_N') d\mathbf{r}_N'.\end{aligned}\quad (12)$$

This is a set of N equations for the N unknown functions $\psi^{(1)}\cdots\psi^{(N)}$. These equations define a wave function of the same form that one uses in the usual LCAO method, namely, the form of Eq. (11). But in the usual applications of the LCAO method one is essentially limited to variational techniques. With the integral equations above, however, one need not limit oneself to variational techniques, although these will undoubtedly be important, but can also use all the other methods which have been developed to deal with integral equations.

If now we expand each of the $\psi^{(i)}(\mathbf{r}_i)$ in spherical harmonics

$$\psi^{(i)}(\mathbf{r}_i) = \sum_{l,m} \psi_{lm}^{(i)}(r_i) Y_{lm}(\Omega_i), \quad (13)$$

then the set of N equations becomes an infinite set of coupled integral equations for the radial parts of the $\psi^{(i)}$, namely, the $\psi_{lm}^{(i)}$. But, and it is a large but, the fact that these partial-wave expansions converge well means that we can to good approximation truncate the set or equations, retaining only the first few partial waves. Moreover, if there is any symmetry in the problem as, e.g., in the configuration of potentials, this can be used to simplify the equations and, as we shall show, they do become practical for computation. Similar remarks apply to the momentum-space counterparts of (12), and since these will turn out to be as useful, and more so, than the coordinate space equations, we derive them now.

To do this we reconsider the i th of Eqs. (12)

$$\psi^{(i)}(\mathbf{r}_i) = - \int \left[\sum_{n=1}^N \psi^{(n)}(\mathbf{r}_n') \right] v_i(\mathbf{r}_i') g_\beta(\mathbf{r}_i, \mathbf{r}_i') d\mathbf{r}_i'. \quad (14)$$

We define the Fourier transform $\phi^{(i)}(\boldsymbol{\lambda})$ of $\psi^{(i)}(\mathbf{r}_i)$ by

$$\phi^{(i)}(\boldsymbol{\lambda}) = \frac{1}{(2\pi)^{3/2}} \int \psi^{(i)}(\mathbf{r}_i) \exp(-i\boldsymbol{\lambda} \cdot \mathbf{r}_i) d\mathbf{r}_i, \quad (15)$$

with the inverse transform

$$\psi^{(i)}(\mathbf{r}_i) = \frac{1}{(2\pi)^{3/2}} \int \phi^{(i)}(\boldsymbol{\lambda}) \exp(i\boldsymbol{\lambda} \cdot \mathbf{r}_i) d\boldsymbol{\lambda}. \quad (16)$$

We multiply Eq. (14) by $\exp(-i\boldsymbol{\lambda} \cdot \mathbf{r}_i)/(2\pi)^{3/2}$ and integrate over \mathbf{r}_i . Also, we observe that the sum over the $\psi^{(n)}$ in this equation can be written

$$\sum_{n=1}^N \psi^{(n)}(\mathbf{r}_n') = \frac{1}{(2\pi)^{3/2}} \sum_{n=1}^N \int \phi^{(n)}(\boldsymbol{\sigma}) \exp(i\boldsymbol{\sigma} \cdot \mathbf{r}_n') d\boldsymbol{\sigma},$$

which is, using Eqs. (1) and (2),

$$\frac{1}{(2\pi)^{3/2}} \sum_{n=1}^N \int \phi^{(n)}(\boldsymbol{\sigma}) \exp[i\boldsymbol{\sigma} \cdot (\mathbf{r}_i' - \mathbf{d}_{in})] d\boldsymbol{\sigma}.$$

Thus Eq. (14) becomes

$$\begin{aligned}\phi^{(i)}(\boldsymbol{\lambda}) &= - \frac{1}{(2\pi)^3} \int \int \int \exp(-i\boldsymbol{\lambda} \cdot \mathbf{r}_i) \\ &\quad \times \left\{ \sum_{n=1}^N \phi^{(n)}(\boldsymbol{\sigma}) \exp[i\boldsymbol{\sigma} \cdot (\mathbf{r}_i' - \mathbf{d}_{in})] \right\} \\ &\quad \times v_i(\mathbf{r}_i') g_\beta(\mathbf{r}_i, \mathbf{r}_i') d\mathbf{r}_i d\mathbf{r}_i' d\boldsymbol{\sigma}. \quad (17)\end{aligned}$$

Now we put the following integral representation for g_β into the right-hand side of (17)

$$g_\beta(\mathbf{r}_i, \mathbf{r}_i') = \frac{1}{(2\pi)^3} \int \frac{\exp[i\boldsymbol{\lambda}' \cdot (\mathbf{r}_i - \mathbf{r}_i')]}{\lambda'^2 + \beta^2} d\boldsymbol{\lambda}'.$$

The integral over $d\mathbf{r}_i$ on the right-hand side then leads to a delta function which enables us to do the $\boldsymbol{\lambda}'$ integration and get

$$\begin{aligned}\phi^{(i)}(\boldsymbol{\lambda}) &= - \frac{1}{(2\pi)^3(\lambda^2 + \beta^2)} \int \int \left\{ \sum_{n=1}^N \phi^{(n)}(\boldsymbol{\sigma}) \exp(-i\boldsymbol{\sigma} \cdot \mathbf{d}_{in}) \right\} \\ &\quad \times v_i(\mathbf{r}_i') \exp[i(\boldsymbol{\sigma} - \boldsymbol{\lambda}) \cdot \mathbf{r}_i'] d\mathbf{r}_i' d\boldsymbol{\sigma}, \quad (18)\end{aligned}$$

or

$$\begin{aligned}\phi^{(i)}(\boldsymbol{\lambda}) &= - \frac{1}{(2\pi)^3(\lambda^2 + \beta^2)} \int \left\{ \sum_{n=1}^N \phi^{(n)}(\boldsymbol{\sigma}) \exp(-i\boldsymbol{\sigma} \cdot \mathbf{d}_{in}) \right\} \\ &\quad \times w^{(i)}(\boldsymbol{\sigma} - \boldsymbol{\lambda}) d\boldsymbol{\sigma}, \quad (19)\end{aligned}$$

where

$$w^{(i)}(\boldsymbol{\sigma} - \boldsymbol{\lambda}) = \int v_i(\mathbf{r}') \exp[i(\boldsymbol{\sigma} - \boldsymbol{\lambda}) \cdot \mathbf{r}'] d\mathbf{r}'. \quad (20)$$

These then are the general equations. They become much less formidable looking when one applies them to particular cases for which there is often some symmetry which may be used to simplify them. For example, the potentials may be identical, or they may be arranged in a symmetric configuration. We return to these points after the next section.

III. PARTIAL-WAVE EXPANSIONS

As we mentioned earlier, an important advantage of the multicenter representation we have adopted is

that we expect the expansions of the wave functions $\phi^{(i)}(\lambda)$ in partial waves to converge well. Now we carry out such partial-wave expansions; the integral equations (19) then become infinite coupled sets of equations which relate the various partial-wave amplitudes one to another.

Consider then Eqs. (19) and (20). Since $v_i(r)$ is spherically symmetric we can easily do the integral over the solid angle of r in Eq. (20) using the plane wave expansion,

$$\exp(i\mathbf{k} \cdot \mathbf{r}) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l j_l(kr) Y_{lm}(\Omega_k) Y_{lm}^*(\Omega_r). \quad (21)$$

We get for $w^{(i)}(\sigma - \lambda)$

$$\sum_{l,m} \phi_{lm}^{(i)}(\lambda) Y_{lm}(\Omega_\lambda) = -\frac{1}{(2\pi)^3(\lambda^2 + \beta^2)} \int \left[\sum_{n=1}^N \sum_{l_1 m_1} \phi_{l_1 m_1}^{(n)}(\sigma) Y_{l_1 m_1}(\Omega_\sigma) \exp(-i\sigma \cdot \mathbf{d}_{in}) \right] \times [4\pi \sum_{l,m} w_l^{(i)}(\sigma, \lambda) Y_{lm}^*(\Omega_\sigma) Y_{lm}(\Omega_\lambda)] d\sigma, \quad (22)$$

or equating coefficients of the $Y_{lm}(\Omega_\lambda)$

$$\phi_{lm}^{(i)}(\lambda) = -\frac{1}{2\pi^2(\lambda^2 + \beta^2)} \int \left[\sum_{n=1}^N \sum_{l_1 m_1} \phi_{l_1 m_1}^{(n)}(\sigma) Y_{l_1 m_1}(\Omega_\sigma) \exp(-i\sigma \cdot \mathbf{d}_{in}) w_l^{(i)}(\sigma, \lambda) Y_{lm}^*(\Omega_\sigma) \right] d\sigma. \quad (23)$$

Now we expand $\exp(-i\sigma \cdot \mathbf{d}_{in})$ by Eq. (21) thereby explicitly introducing the interparticle distance d_{in}

$$\exp(-i\sigma \cdot \mathbf{d}_{in}) = (4\pi) \sum_{l_2 m_2} (-i)^{l_2} j_{l_2}(\sigma d_{in}) Y_{l_2 m_2}^*(\Omega_\sigma) Y_{l_2 m_2}(\Omega_{d_{in}}),$$

and we get

$$\phi_{lm}^{(i)}(\lambda) = -\frac{2}{\pi(\lambda^2 + \beta^2)} \int \sum_{n=1}^N \sum_{l_1 m_1} \sum_{l_2 m_2} [\phi_{l_1 m_1}^{(n)}(\sigma) Y_{l_1 m_1}(\Omega_\sigma) (-i)^{l_2} j_{l_2}(\sigma d_{in}) \times Y_{l_2 m_2}^*(\Omega_\sigma) Y_{l_2 m_2}(\Omega_{d_{in}}) w_l^{(i)}(\sigma, \lambda) Y_{lm}^*(\Omega_\sigma)] \sigma^2 d\sigma d\Omega_\sigma. \quad (24)$$

Now we can do the integration over the three spherical harmonics, using³

$$\int Y_{lm} Y_{l_1 m_1} Y_{l_2 m_2} d\Omega = A(lm l_1 m_1 l_2 m_2), \quad (25)$$

where

$$A(lm l_1 m_1 l_2 m_2) = \left[\frac{(2l+1)(2l_1+1)(2l_2+1)}{4\pi} \right]^{1/2} \begin{pmatrix} l & l_1 & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l_1 & l_2 \\ m & m_1 & m_2 \end{pmatrix}. \quad (26)$$

Here $\begin{pmatrix} l & l_1 & l_2 \\ m & m_1 & m_2 \end{pmatrix}$ is a 3- j coefficient and we need to use

$$Y_{lm}^* = (-)^m Y_{l,-m}.$$

Thus finally the i th of the N integral equations becomes

$$\phi_{lm}^{(i)}(\lambda) = -\frac{2}{\pi(\lambda^2 + \beta^2)} \int_0^\infty \sum_{n=1}^N \sum_{l_1 m_1} \sum_{l_2 m_2} A(l-m l_1 m_1 l_2 -m_2) (i)^{l_2} \times (-)^{m+m_2+l_2} w_l^{(i)}(\sigma, \lambda) \phi_{l_1 m_1}^{(n)}(\sigma) j_{l_2}(\sigma d_{in}) Y_{l_2 m_2}(\Omega_{d_{in}}) \sigma^2 d\sigma. \quad (27)$$

² For brevity, henceforth we use $\Sigma_{l,m}$ to mean $\Sigma_{l=0}^\infty \Sigma_{m=-l}^l$.

³ A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957), p. 63.

IV. CYCLIC SYSTEMS

A. The Specialized Equations

The integral equations derived above are not very transparent, written as they are for the most general case of an arbitrary number of possibly unlike potentials arranged in an arbitrary configuration. In this section we apply them to some concrete cases and discuss their solution to get a better idea of their practicality.

We begin with the problem of the ground state of a cyclic system, i.e., of a particle bound to *identical* potentials in a symmetric polygonal configuration, e.g., equilateral triangle, square, pentagon, etc., and as a degenerate case of a plane polygon, a particle bound to two potentials a distance d apart. The momentum-space wave function $\phi^{(i)}(\lambda)$ is defined as the Fourier transform of a wave function $\psi^{(i)}(\mathbf{r}_i)$ where \mathbf{r}_i is itself defined with respect to the coordinate system associated with the i th potential. Now for every potential, we choose the orientation of the associated coordinate system in an identical way (a point to which we shall return) and consider the ground state, or states with the symmetry of the ground state. Then the basic equations (19) simplify considerably. First we observe that when all the potentials are identical, the superscript on $w^{(i)}(\sigma-\lambda)$ is superfluous and we can simply call it $w(\sigma-\lambda)$. Similarly, if all the potentials are identical and all the coordinate systems are chosen symmetrically and we are looking for the ground state of the system, then all the $\psi^{(i)}(\mathbf{r}_i)$ will have the same functional form, i.e., $\psi^{(1)}$ will be the same function of \mathbf{r}_1 as $\psi^{(2)}$ is of \mathbf{r}_2 , etc. In short, the superscripts on these functions will be superfluous and we can simply call them all ψ . As a consequence, a similar remark applies to the functions $\phi^{(i)}(\lambda)$, which we shall call $\phi(\lambda)$. Then $\phi(\sigma)$ factors out of the summation over n in Eq. (19). Also, this equation was written for the i th potential, but since all the potentials are identical it does not make any difference how we number them, and it is convenient to take $i=1$. Factoring $\phi(\sigma)$ out of the sum, the N integral Eqs. (19) become redundant and reduce to a single one for determining the single unknown function $\phi(\lambda)$,

$$\phi(\lambda) = -\frac{1}{(2\pi)^3(\lambda^2 + \beta^2)} \int \left[\sum_{n=1}^N \exp(-i\sigma \cdot \mathbf{d}_{1n}) \right] \times \phi(\sigma) w(\sigma - \lambda) d\sigma. \quad (31)$$

This equation is like the momentum space equation for a particle bound to a single potential, except for

$$\phi_{lm}(\lambda) = -\frac{1}{2\pi^2(\lambda^2 + \beta^2)} \int_0^\infty w_l(\sigma, \lambda) \left[\phi_{lm}(\sigma) + \sum_{l_2 m_2} \sum_{l_1 m_1} (-)^m A(l-m, l_1 m_1, l_2 m_2) \phi_{l_2 m_2}(\sigma) S_{l_1 m_1}(\sigma, 'd') \right] \sigma^2 d\sigma. \quad (38)$$

These then are the desired equations for the symmetric states of the symmetric configurations described above.

B. The Truncated S-Wave Equations

As we have remarked previously, we expect that for the ground state, Eq. (38) can be truncated, i.e.,

the presence of the "structure factor" $S(\sigma, \mathbf{d}_{12} \cdots \mathbf{d}_{1N})$ in the integrand

$$S(\sigma, \mathbf{d}_{12} \cdots \mathbf{d}_{1N}) = \sum_{n=1}^N \exp(-i\sigma \cdot \mathbf{d}_{1n}). \quad (32)$$

This is the main reason for the fact that the momentum space equations are more useful than the coordinate ones, i.e., they enable us (at least for cyclical systems) to break the problem up into two parts: the structure factor which depends only on the configuration of potentials, and the function $w(\sigma-\lambda)$ which depends only on the individual potential shape.

It is convenient to expand the structure factor in spherical harmonics of Ω_σ . We have, using Eq. (21),

$$S(\sigma, \mathbf{d}_{12} \cdots \mathbf{d}_{1N}) = 1 + 4\pi \sum_{n=2}^N \sum_{l,m} (-i)^l j_l(\sigma d_{1n}) \times Y_{lm}(\Omega_\sigma) Y_{lm}^*(\Omega_{d_{1n}}). \quad (33)$$

For brevity, we define new quantities $S_{lm}(\sigma, 'd')$, where ' d ' is shorthand for $d_{12} \cdots d_{1N}$, by the equations

$$S(\sigma, \mathbf{d}_{12} \cdots \mathbf{d}_{1N}) = 1 + \sum_{l,m} S_{lm}(\sigma, 'd') Y_{lm}(\Omega_\sigma), \quad (34)$$

$$S_{lm}(\sigma, 'd') = 4\pi \sum_{n=2}^N (-i)^l j_l(\sigma d_{1n}) Y_{lm}^*(\Omega_{d_{1n}}). \quad (35)$$

In Appendix I we calculate, as an illustrative example, some of the elements of the structure factor for a square configuration of potentials.

Using Eq. (34) for the expansion of the structure factor in spherical harmonics, we can now write a set of coupled equations for the partial-wave amplitudes $\phi_{lm}(\lambda)$. These equations will, of course, be special cases of the previous ones, but since the present case is especially simple, it is convenient to write the equations anew so that the elements of the structure factor appear explicitly. Thus, we put the expansion (34) for the structure factor into Eq. (31) along with the expansions for $\phi(\lambda)$ and $w(\sigma-\lambda)$,

$$\phi(\lambda) = \sum_{l,m} \phi_{lm}(\lambda) Y_{lm}(\Omega_\lambda), \quad (36)$$

and

$$w(\sigma-\lambda) = 4\pi \sum w_l(\sigma, \lambda) Y_{lm}^*(\Omega_\sigma) Y_{lm}(\Omega_\lambda). \quad (37)$$

Equating coefficients of $Y_{lm}(\Omega_\lambda)$ on both sides of the resulting equation, we get

that all but the first few ϕ_{lm} are negligible. In fact, we not only expect this to be approximately correct in general, but know that it must be exact in the two limits in which the potentials coalesce ($d_{1n} \rightarrow 0$) and when they become widely separated ($d_{1n} \rightarrow \infty$), in both of which cases the ground-state wave function

contains only S waves, $l=0$. Thus there certainly is a range of the d_{1n} for which it is a good first approximation to take, as a starting point, Eq. (38) with only $\phi_{00}(\lambda)$ assumed different from zero. A natural program then is to try to solve for $\phi_{00}(\lambda)$, and then to use this solution to estimate the neglected higher order partial waves. This is the program we discuss; in this subsection we concentrate on solving for ϕ_{00} .

We make the approximation therefore, of taking $l=0$ in Eq. (38) and retaining only $l_2=0$ in the sum on the right-hand side. This implies that only the term $l_1=0$ survives the sum on l_1 and the integral equation becomes the relatively simple one

$$\phi_{00}(\lambda) = -\frac{1}{2\pi^2(\lambda^2 + \beta^2)} \int_0^\infty w_0(\sigma, \lambda) \phi_{00}(\sigma) \times [1 + S_{00}(\sigma, 'd')] \sigma^2 d\sigma. \quad (39)$$

The factor $1 + S_{00}(\sigma, 'd')$ characterizes the particular polygon we deal with. Simple calculations, analogous to the one in the Appendix, give for $1 + S_{00}$ the following expressions for the configurations specified; here d is the polygon side.

$$\begin{aligned} 1 + j_0(\sigma d), & \quad \text{linear;} \\ 1 + 2j_0(\sigma d), & \quad \text{equilateral triangle;} \\ 1 + 2j_0(\sigma d) + j_0[\sigma(2d)^{1/2}], & \quad \text{square;} \\ 1 + 2j_0(\sigma d) + 2j_0[2\sigma d \cos(\pi/5)], & \quad \text{pentagon.} \end{aligned}$$

Equation (39) differs from the corresponding $l=0$ momentum space equation for a single potential only through the fact that $1 + S_{00}(\sigma, 'd')$ appears in the integrand. In fact, when d becomes infinite, $S_{00}(\sigma, 'd')$ goes to zero, and we have just the integral equation for the ground S state in a single potential. When d goes to zero, $1 + S_{00}(\sigma, 'd')$ becomes equal to N , and we have the problem of a particle bound in an S state to a potential which is N times as strong as the single one. Thus in a qualitative way, we see that some average value of $[1 + S_{00}(\sigma, 'd')]$ is the effective strength of the potential, or if we are dealing with Coulomb potentials, is the "effective nuclear charge."

We now discuss possible methods for the solution of the integral Eq. (39). First we rewrite it with an eye toward symmetrizing the kernel

$$\phi_{00}(\lambda) [1 + S_{00}(\lambda, 'd')]^{1/2} = -\frac{1}{2\pi^2(\lambda^2 + \beta^2)} \int_0^\infty w_0(\sigma, \lambda) [1 + S_{00}(\sigma, 'd')]^{1/2} [1 + S_{00}(\lambda, 'd')]^{1/2} \phi_{00}(\sigma) [1 + S_{00}(\sigma, 'd')]^{1/2} \sigma^2 d\sigma.$$

Now we define "effective" quantities ϕ_{eff} and w_{eff} :

$$\phi_{\text{eff}}(\lambda) = \phi_{00}(\lambda) [1 + S_{00}(\lambda, 'd')]^{1/2}, \quad (40)$$

$$w_{\text{eff}}(\sigma, \lambda) = w_0(\sigma, \lambda) [1 + S_{00}(\lambda, 'd')]^{1/2} \times [1 + S_{00}(\sigma, 'd')]^{1/2}. \quad (41)$$

We then have

$$\beta^2 = -\left(\int_0^\infty \phi_{\text{eff}}^2(\lambda) \lambda^2 d\lambda + \frac{1}{2\pi^2} \int_0^\infty \int_0^\infty \phi_{\text{eff}}(\sigma) \phi_{\text{eff}}(\lambda) w_{\text{eff}}(\sigma, \lambda) \sigma^2 \lambda^2 d\sigma d\lambda \right) / \int_0^\infty \phi_{\text{eff}}^2(\lambda) \lambda^2 d\lambda.$$

If $\phi_{\text{eff}}(\lambda)$ is unknown, this expression is a variational one, and it can be used then with an *approximate* $\phi_{\text{eff}}(\lambda)$ to give an energy β^2 with an error of higher "order" than appears in ϕ_{eff} itself. Formally, at least, this variational principle has the advantage over the usual multicenter formulation of the variational principle that only one double integral is involved, and not the usual multiplicity of multicenter integrals.

One need not be limited to a variational principle, however. For since Eq. (42) is essentially the momentum space equation for an effective "potential" $w_{\text{eff}}(\sigma, \lambda)$ we can transform it back to coordinate space, and exhibit the effective potential in its usual form as an ordinary potential in space. This is an attractive possibility, so we shall discuss it in detail, along with some minor difficulties associated with it.

We first ask how we can reconstruct the potential

$$\phi_{\text{eff}}(\lambda) = -\frac{1}{2\pi^2(\lambda^2 + \beta^2)} \int_0^\infty w_{\text{eff}}(\sigma, \lambda) \phi_{\text{eff}}(\sigma) \sigma^2 d\sigma. \quad (42)$$

With the equation in this symmetrical form we can now apply any of the usual methods for integral equations of this type. For example, for the ground state, we have the following variational principle. If we knew $\phi_{\text{eff}}(\lambda)$ we could evaluate the energy from

$v(r)$ from a knowledge of $w_0(\sigma, \lambda)$, defined by Eq. (23), viz.,

$$w_0(\sigma, \lambda) = 4\pi \int_0^\infty j_0(\sigma r) v(r) j_0(\lambda r) r^2 dr.$$

The answer is that we can invert this using the basic theorem on Fourier-Bessel transforms,⁴ and get

$$v(r) j_0(\lambda r) = \frac{1}{2\pi^2} \int_0^\infty w_0(\sigma, \lambda) j_0(\sigma r) \sigma^2 d\sigma.$$

In particular, if we set $\lambda=0$, we get simply

$$v(r) = \frac{1}{2\pi^2} \int_0^\infty w_0(\sigma, 0) j_0(\sigma r) \sigma^2 d\sigma. \quad (43)$$

⁴ If $f(k) = (2/\pi)^{1/2} \int_0^\infty g(s) j_0(ks) s^2 ds$ then $g(s) = (2/\pi)^{1/2} \int_0^\infty f(k) \times j_0(ks) k^2 dk$.

Applying these last results to w_{eff} we get the effective space potential that we seek, and which we call $v_{\text{eff}}(r)$:

$$v_{\text{eff}}(r) = \frac{\sqrt{2}}{2\pi^2} \int_0^\infty w_0(\sigma, 0) j_0(\sigma r) [1 + j_0(\sigma d)]^{1/2} \sigma^2 d\sigma. \quad (44)$$

It should be noticed, and this is one of the difficulties mentioned above, that this last formula does not hold in the limit $d \rightarrow \infty$. The reason is that in it we have set $\lambda = 0$, and the value of $[1 + j_0(\lambda d)]^{1/2}$ for $\lambda \rightarrow 0$, $d \rightarrow \infty$ depends on the order in which we take these limits, it being $\sqrt{2}$ for the order written above, and unity for the order, $d \rightarrow \infty$, $\lambda \rightarrow 0$. However, the result (44) can be applied for d different from infinity. Consider for example the screened Coulomb potential

$$v(r) = -2e^{-\alpha r}/r,$$

for which we have

$$w_0(\sigma, 0) = -8\pi/(\sigma^2 + \alpha^2),$$

whence

$$v_{\text{eff}}(r) = -\frac{4\sqrt{2}}{\pi} \int_0^\infty \frac{\sigma^2}{\sigma^2 + \alpha^2} j_0(\sigma r) [1 + j_0(\sigma d)]^{1/2} \sigma^2 d\sigma. \quad (45)$$

Because of the square root in the integrand, this integral is not easy to solve as it stands. However, since $j_0(\sigma d)$ is less than one everywhere except at the origin, and since the other factor in the integrand $[\sigma^2/(\sigma^2 + \alpha^2)] \times j_0(\sigma r)$ goes to zero fairly rapidly at the origin, it seems permissible to expand the square root and integrate term by term

$$v_{\text{eff}}(r) = -\frac{4\sqrt{2}}{\pi} \int_0^\infty \frac{\sigma^2}{\sigma^2 + \alpha^2} j_0(\sigma r) \times \left(1 + \frac{j_0(\sigma d)}{2} - \frac{j_0^2(\sigma d)}{8} + \dots \right) d\sigma.$$

Doing the integrations for the three terms written above, we get the approximation

$$v_{\text{eff}}(r) \approx -(2/r) [e^{-\alpha r} + (1/4\alpha d)(e^{-\alpha(r+d)} - e^{-\alpha|r-d|}) - (1/32d^2\alpha^2)(e^{-\alpha(r+2d)} + e^{-\alpha|r-2d|} - 2e^{-\alpha r}) + \dots]. \quad (46)$$

It should be noted that we cannot let α go to zero in this last expression, since it then diverges. The reason is that for $\alpha \rightarrow 0$ it is not legitimate to expand the square root in the integrand of (44). Thus for the Coulomb potential the effective potential is defined directly by Eq. (45).

Now we consider a final method for the solution of Eq. (39), and one which we shall work out in some detail. As we have observed previously, we could solve Eq. (39) if the factor $1 + S_{00}(\sigma, d')$, which plays the role of an "effective nuclear charge" were in fact a constant and not a function of σ . This suggests that if we were to define an average value of this quantity, and if further

it were a good approximation to replace $1 + S_{00}(\sigma', d')$ in the integrand by this average value, which we shall call Z' and which we shall shortly define more precisely, then we would easily have an approximate solution of Eq. (39). For this equation would then become the approximate one

$$\phi_{00}(\lambda) = -\frac{Z'}{2\pi^2(\lambda^2 + \beta^2)} \int_0^\infty w_0(\sigma, \lambda) \phi_{00}(\sigma) \sigma^2 d\sigma, \quad (47)$$

and this is just like the equation for the S state of a particle moving in a spherical well of shape characterized by $w_0(\sigma, \lambda)$. In particular, it is soluble if $w_0(\sigma, \lambda)$ corresponds to a Coulomb potential, and this is the case we treat.

We discuss in detail the case $N=2$, the hydrogen molecule ion; the results for higher N can then be written down immediately by analogy. We use atomic units in which $\beta^2 = 2|E|$ and $v(r) = -(2/r)$. Now for the Coulomb potential we know the exact solution for the lowest state of the integral equation (47). The eigenvalue is

$$\beta = Z' \quad \text{or} \quad |E| = (Z'^2/2), \quad (48)$$

and the eigenfunction is

$$\phi_{00}(\lambda) = 1/(\lambda^2 + Z'^2)^2. \quad (49)$$

Using these results, we shall now derive an approximate solution of Eq. (39); in fact, we shall derive this solution in two different ways to throw as much light as we can on the nature of the approximation.

For the first derivation we begin by defining Z' as the average value of $1 + j_0(\sigma d)$, the average being calculated with respect to the true wave function ϕ_{00} , i.e., we write

$$Z' = \int_0^\infty [1 + j_0(\sigma d)] \phi_{00}(\sigma) d\sigma / \int_0^\infty \phi_{00}(\sigma) d\sigma. \quad (50)$$

Now this definition is a circular one, in that we do not know the true wave functions $\phi_{00}(\sigma)$. However, we can make the definition fruitful if we consistently use the assumption that the solution of Eq. (39) is approximated by the solution of Eq. (47), which involves the (as yet unknown) effective charge Z' . For we then simply put the expression (49) into the right-hand side of Eq. (50) as an approximation to ϕ_{00} and we get a transcendental equation for Z' . Thus Eq. (50) becomes

$$Z' = \int_0^\infty [1 + j_0(\sigma d)] \frac{d\sigma}{(\sigma^2 + Z'^2)^2} / \int_0^\infty \frac{d\sigma}{(\sigma^2 + Z'^2)^2} = \frac{4Z'^3}{\pi} \int_0^\infty [1 + j_0(\sigma d)] \frac{d\sigma}{(\sigma^2 + Z'^2)^2}, \quad (51)$$

and this is an equation which defines Z' and hence, from Eq. (48), the energy.

Before we give numerical results based on this equation, we shall derive it in another way, as follows. We observe that if we *knew* the wave function $\phi_{00}(\lambda)$ which is the solution of Eq. (39) we could conveniently calculate the energy by putting λ in it equal to some particular value, a convenient value being $\lambda=0$. This would then give (again for $N=2$)

$$\beta^2 = - \int_0^\infty [1 + j_0(\sigma d)] w_0(\sigma, 0) \phi_{00}(\sigma) \sigma^2 d\sigma / 2\pi^2 \phi_{00}(0).$$

Using the definition (20) for w_0 we get for the Coulomb potential

$$w_0(\sigma, 0) = -8\pi/\sigma^2,$$

whence we have

$$\beta^2 = + \frac{4}{\pi} \int_0^\infty [1 + j_0(\sigma d)] \phi_{00}(\sigma) d\sigma / \phi_{00}(0). \quad (52)$$

If now we again use the assumption that the solution

$$d = \frac{\zeta}{1 + (2/\zeta)[2 - e^{-\zeta}(2 + \zeta)]}, \quad \text{triangle};$$

$$d = \frac{\zeta}{1 + (2/\zeta)[2 - e^{-\zeta}(2 + \zeta)] + (1/\zeta\sqrt{2})[2 - \exp(-\zeta\sqrt{2})(2 + \zeta\sqrt{2})]}, \quad \text{square}.$$

For the diatomic case, we can compare our results with the exact ones derived by Bates, Ledsham, and Stewart⁶ for the hydrogen molecule ion. This is done in Fig. 3. In comparing our result with the exact one, it is important to remember that our results are approximate for two different reasons. The first is the approximation that has been made in truncating the general equations (38) to arrive at the *S*-wave-only equation (39); second is the approximation we made in finding the solution of this equation. We know the first approximation gets better as d becomes either very small or very large; hence, we expect that the error exhibited in

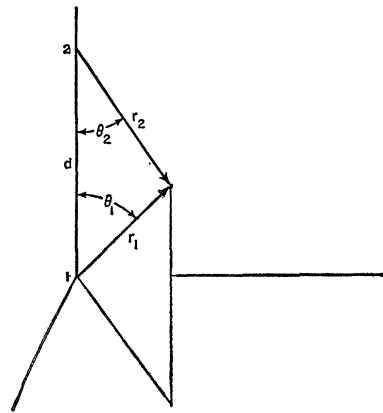


FIG. 1. Coordinate systems for two identical potentials.

of Eq. (39) is approximated by that of Eq. (47), namely that $\phi_{00}(\sigma)$ is $1/(\sigma^2 + \beta^2)^2$ and that $\beta = Z'$, we see that this equation becomes exactly the same as Eq. (51).

The integral in Eq. (51) is elementary and upon doing it the equation becomes one for Z' , and hence the energy, as a function of d . We get

$$Z' = 1 + 1/(Z'd)[2 - e^{-Z'd}(2 + Z'd)]. \quad (53)$$

Note that Eq. (53) gives the correct value of Z' in the two limits $d \rightarrow 0$ and $d \rightarrow \infty$.

Practically, it is easy to calculate energies from Eq. (53). We rewrite it in terms of the parameter $\zeta = Z'd$ to get

$$d = \frac{\zeta}{1 + (1/\zeta)[2 - e^{-\zeta}(2 + \zeta)]},$$

from which for a given ζ , d can be found. Analogous equations for the triangular and square configurations are

Fig. 3 is for d less than $1/2$, say, or greater than 3 or 4, mainly due to the approximate solution of Eq. (39).

C. The "Polarization" Amplitude

Now we turn to the second part of the program discussed above, namely, the estimation of the *P*-wave or "polarization" contribution to the orbitals. We shall work this out for $N=2$, the hydrogen molecule ion, in which case the results can be compared with previous ones, but the same procedure would hold for $N>2$.

We begin then by writing out Eq. (38) for $N=2$, including both the $l=0$ and $l=1$ partial waves (now assuming that still higher ones are negligible). We take the two potentials to be a distance d apart. For the ground state, the wave function is cylindrically symmetric, so that it is convenient, with reference to Fig. 1, to put the first potential at the origin and the second at $z=d$ on the z axis. At each of the potentials we have a separate coordinate system and Eq. (38) implies that we have chosen the coordinates \mathbf{r}_1 and \mathbf{r}_2 in a symmetric way. This will be so if we define the coordinates as in Fig. 1, where both θ_1 and θ_2 are chosen to be *interior* angles. Then, we set $m=0$ in Eq. (38) and write them out for $l=0$ and for $l=1$. To reduce the number of subscripts, we introduce a slightly different notation for this case. We call $\phi_{00}(\lambda)$ and $\phi_{10}(\lambda)$, the only two assumed nonzero amplitudes, $\phi_0(\lambda)$ and $\phi_1(\lambda)$. Referring to the summation on the right-hand side of

⁶ D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. A246, 215 (1953).

Eq. (38), if $m=0$ and m_2 is always zero, then it follows from the properties of $A(lm_1m_2m_3)$ that m_1 must be

$$\phi_0(\lambda) = -\frac{1}{2\pi^2(\lambda^2+\beta^2)} \int_0^\infty w_0(\sigma, \lambda) [\phi_0(\sigma) + \phi_0(\sigma) \sum_{l_1} A(0l_10)S_{l_10}(\sigma, 'd') + \phi_1(\sigma) \sum_{l_1} A(0l_11)S_{l_10}(\sigma, 'd')] \sigma^2 d\sigma, \quad (54)$$

$$\phi_1(\lambda) = -\frac{1}{2\pi^2(\lambda^2+\beta^2)} \int_0^\infty w_1(\sigma, \lambda) [\phi_1(\sigma) + \phi_0(\sigma) \sum_{l_1} A(1l_10)S_{l_10}(\sigma, 'd') + \phi_1(\sigma) \sum_{l_1} A(1l_11)S_{l_10}(\sigma, 'd')] \sigma^2 d\sigma. \quad (55)$$

Now the coefficients $A(l_1l_2l_3)$ are zero unless the "triangular equality" is satisfied, i.e., unless, considering l_1, l_2 and l_3 as angular momenta, their magnitudes are such that two of them could be coupled by the vector-coupling model to give the third. Using this property of the A 's and others which derive from the definitions of the 3- j coefficients as given in reference 3, the two equations become

$$\phi_0(\lambda) = -\frac{1}{2\pi^2(\lambda^2+\beta^2)} \int_0^\infty w_0(\sigma, \lambda) \{ \phi_0(\sigma) [1 + j_0(\sigma d)] + i\phi_1(\sigma) j_1(\sigma d) \} \sigma^2 d\sigma, \quad (56)$$

$$\phi_1(\lambda) = -\frac{1}{2\pi^2(\lambda^2+\beta^2)} \int_0^\infty w_1(\sigma, \lambda) \{ \phi_1(\sigma) [1 + j_0(\sigma d)] - i\sqrt{3}\phi_0(\sigma) j_1(\sigma d) - 2\phi_1(\sigma) j_2(\sigma d) \} \sigma^2 d\sigma. \quad (57)$$

Now we can use these equations in the way suggested above. That is, in the last of these equations, we assume that ϕ_1 is small compared with ϕ_0 , and keep only ϕ_0 in

zero and it is convenient to define $A(0l_10l_20) \equiv A(l_1l_2)$. Equations (38) written out for $l=0$ and $l=1$ then are

the right-hand side to get an estimate of ϕ_1

$$\phi_1(\lambda) \approx \frac{i\sqrt{3}}{2\pi^2(\lambda^2+\beta^2)} \int_0^\infty w_1(\sigma, \lambda) \phi_0(\sigma) j_1(\sigma d) \sigma^2 d\sigma. \quad (58)$$

We note that this equation confirms the fact that ϕ_1 vanishes for d going both to zero and to infinity. We also note that having estimated ϕ_1 , we can go back and use it in Eq. (56) to improve our original calculation of ϕ_0 .

Now we discuss the integral in Eq. (58). For the Coulomb potential $v(r) = -2/r$ we have

$$w_1(\sigma, \lambda) = -8\pi \int_0^\infty j_1(\sigma r) j_1(\lambda r) r dr.$$

The last integral is a standard one in the theory of Bessel functions, and gives

$$w_1(\sigma, \lambda) = -(4\pi/\sigma\lambda) Q_1[(\sigma^2+\lambda^2)/2\sigma\lambda], \quad (59)$$

where Q_1 is a Legendre polynomial of the second kind,

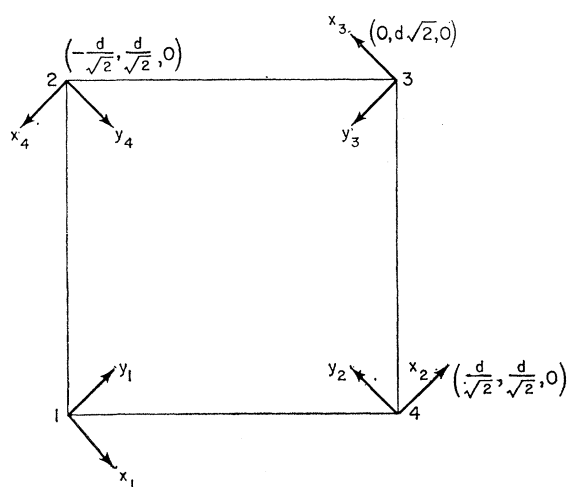


FIG. 2. Illustrating one possible choice of individual coordinate systems for a square configuration of potentials. At each of the corners of the square there is a separate coordinate system, each oriented with respect to its corner in an identical way. The parentheses at corners 2, 3, and 4 give the coordinates of that corner in the x_1, y_1, z_1 system.

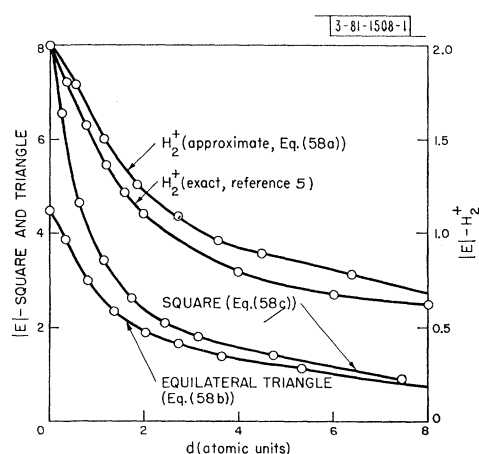


FIG. 3. Approximate ground-state binding energy E using S -wave orbitals only, for an electron bound to two Coulomb potentials (hydrogen molecule ion), and the exact results from reference 5. Distances d and energies E (right-hand ordinate) in atomic units. Also, approximate energies (left-hand ordinate) for electron bound to a triangular and to a square configuration of Coulomb potentials, again with S -wave orbitals.

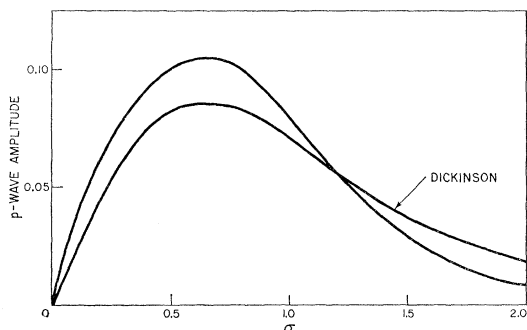


FIG. 4. The P -wave momentum space orbital $i\phi_1(\sigma)$ as calculated from Eq. (58) and from the "best" S -wave orbital function $\phi_0(\sigma) = Z'^4/(Z'^2 + \sigma^2)^2$ with $Z' = 1.220$. This function is normalized to unity at $\sigma = 0$. The curve labeled "Dickinson" is the corresponding function as calculated by Dickinson, i.e., it is the factor of $i \cos \theta$ in the expression for the "best" momentum space orbital, which is (S -wave part also normalized to unity at the origin)

$$\frac{Z'^4}{(Z'^2 + \sigma^2)^2} + i b \frac{64}{\sqrt{3} Z''} \left(\frac{Z'}{Z''} \right)^{5/2} \frac{\sigma Z''^6}{(Z'^2 + 4\lambda^2)^2} \cos \theta,$$

with $b = 0.145$, $Z' = 1.247$, $Z'' = 2.868$.

which is, for $x > 1$

$$Q_1(x) = (x/2) \ln[(x+1)/(x-1)] - 1. \quad (60)$$

For $x > 1$ we have the expansion

$$Q_1(x) = (1/x^2)(1/3 + 1/5x^2 + 1/7x^4 + \dots). \quad (61)$$

For $\phi_0(\sigma)$ the solution of the S -wave equations, we take as an approximation a function of the form we have discussed, viz.,

$$\phi_0(\sigma) = Z'^4/(\sigma^2 + Z'^2)^2. \quad (62)$$

This corresponds to a hydrogenlike S -wave orbital with effective nuclear charge Z' .

We have not succeeded in evaluating (58) with (62) and the general expression (59): The logarithm in the integrand causes difficulty. However, one can get a series expansion by combining (61) and (59), and the integrals that arise can be done, although the results are clumsy. Unfortunately, the resulting series does not converge well in general, so that it is not satisfactory for accurate computation. However, keeping as a rough approximation only the first term in (61) does give an expression with the correct qualitative behavior and order of magnitude and one which is, therefore, useful for general insight. With this approximation we have

$$\phi_1(\lambda) \approx \frac{8i\lambda}{\pi\sqrt{3}(\lambda^2 + \beta^2)} \int_0^\infty \frac{j_1(\sigma d)\sigma^3 d\sigma}{(\sigma^2 + \lambda^2)^2(\sigma^2 + Z'^2)^2},$$

whence

$$\phi_1(\lambda) \approx \frac{i8\lambda}{\sqrt{3}(\lambda^2 + \beta^2)(Z'^2 - \lambda^2)^3} \left[e^{-\lambda d} \left(\frac{2}{d^2} - \frac{(Z'^2 - \lambda^2)}{2} + \frac{2\lambda}{d} \right) - e^{-Z' d} \left(\frac{2}{d^2} + \frac{(Z'^2 - \lambda^2)}{2} + \frac{2Z'}{d} \right) \right].$$

From this we see that $\phi_1(\lambda)$ vanishes exponentially with d for large d , and linearly for small d . Note that this function is well behaved at $\lambda = Z'$, despite the superficial appearance of a singularity there.

For accuracy then, we have calculated the integral in (58) numerically. To compare with previous work, we have done this for $d = 2.0$, the equilibrium internuclear distance for the hydrogen molecule ion. For this case there are variational calculations by Dickinson⁶ with an LCAO function of the type we are considering. To clarify this comparison, we choose not the Z' we have found in the previous subsection, but the one that is variationally best; this is $Z' = 1.22$. The results are given in Fig. 4. We see that the Dickinson polarization term, as calculated variationally, and the present one as calculated from the techniques of this paper, are in substantial agreement. Thus, the energy we would get if we were now to use the present function in a variational calculation would be very close to Dickinson's, which in turn is very close to the correct value as found by an exact solution of the problem. In this connection, one should note that the energy is not very sensitive to the shape of the Dickinson polarization function and that for slightly different values of the parameters in it, one gets almost as good an energy value but with a function which agrees even more closely with the one we have calculated.

V. DISCUSSION

In this section we discuss the salient features of the method we have described.

The main point of this paper has been to try to find a way of treating the multicenter problem that maintains the advantage of the usual LCAO method, in that it represents the wave function in a natural and rapidly convergent form [namely, the form of Eq. (11)] but which is not limited, as is the usual LCAO method, to determining the wave functions solely by variational techniques. Correspondingly, we consider that our main results are the sets of integral equations (19), which do define wave functions of the required form. We have presented the approximate solution (49) for the special case of the ground state in polygonal configurations simply to show that at least in one case the integral equations are tractable, but we do not consider this to be the last word on the subject. There are other techniques for solution available in addition to the simple one that we have presented, and techniques⁷ which are also applicable to more complicated cases; for example, to the coupled Eqs. (54) and (55). These remain to be explored.

⁶ B. N. Dickinson, J. Chem. Phys. **1**, 317 (1933).

⁷ See, for example, Z. Kopal, *Numerical Analysis* (John Wiley & Sons, New York, 1955); P. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1956); L. V. Kantorovich and V. I. Krylov, *Approximate Methods of Higher Analysis* (Interscience Publishers, Inc., New York, 1958).

In this connection we would like to emphasize the possibilities of iteration, in which one starts from an approximate wave function and then corrects it systematically. We have, of course, done this to a limited degree in calculating the polarization terms for the hydrogen molecule ion from the approximate S -wave orbitals. But given a little luck with convergence there seems to be no reason that one could not, using computers, carry this to much better accuracy. Thus having calculated the polarization amplitude as we have done, one could go back and see its effect on the S -wave orbitals, using Eq. (56), then recalculate the polarization amplitudes with the corrected S -wave functions, and so, hopefully, arrive at a quite accurate wave function and energy. Similar remarks would, of course, apply to more complicated problems.

It is perhaps worth mentioning that it is, in a way, accidental that the equations we finally find most useful are those in momentum space instead of coordinate space. It just so happens that the momentum equations are simpler to deal with once one has chosen to represent the wave function in the form of Eq. (11). But the use of momentum space is secondary to the main point of the paper, which rather is to take the form (11) seriously and at the same time to try to throw off the yoke of the variational principle. In this connection, it is also worth mentioning that, although some of our equations are superficially similar to those derived by McWeeny,⁸ who has used momentum space for treating the H_2^+ molecule, the present method and McWeeny's are quite different. The crucial difference is, of course, that we deal with the "decomposed" integral equations for the individual orbitals, which must then be combined according to Eq. (11) to give the total wave function. On the other hand, the integral equation that McWeeny directly uses is the quite different one for the total momentum space wave function.

APPENDIX I

Calculation of Structure Factor for a Square Configuration

As an illustration, we derive some of the elements of the structure factor for a square configuration of potentials. With reference to the discussion in Sec. I,

⁸ R. McWeeny, Proc. Phys. Soc. London A62, 519 (1949).

we take the first potential at the origin of a general coordinate system. Moreover, we take the coordinate system \mathbf{r}_1 as shown in Fig. 2, with the y_1 axis along the diagonal and the z axis out of the plane of the paper, and with a similar coordinate system at each of the other three corners of the square. The elements S_{lm} of the structure factor are defined by

$$S_{lm} = (-i)^l \sum_{n=2}^4 j_l(\sigma d_{1n}) Y_{lm}(\Omega_{d_{1n}}).$$

Now the coordinates of the point 2 in the \mathbf{r}_1 system are $(-d/\sqrt{2}, d/\sqrt{2}, 0)$, of point 3 are $(0, d\sqrt{2}, 0)$ and of point 4 are $(d/\sqrt{2}, d/\sqrt{2}, 0)$; the distances that enter into the arguments of the Bessel functions are $d_{12}=d$, $d_{13}=d\sqrt{2}$, $d_{14}=d$. With these results, and the expressions for the spherical harmonics in terms of vector components, e.g.

$$Y_{00} = 1/(4\pi)^{1/2}, \quad Y_{10} = \frac{1}{2}(3/\pi)^{1/2}(z/r), \\ Y_{1\pm 1} = \pm \frac{1}{2}(3/2\pi)^{1/2}[(x \pm iy)/r],$$

we can evaluate the structure factor immediately. For example, we have

$$S_{00} = \sum_{n=2}^4 j_0(\sigma d_{1n}) Y_{00}(\Omega_{d_{1n}}) \\ = [2j_0(\sigma d) + j_0(\sigma d\sqrt{2})]/(4\pi)^{1/2}, \\ S_{11} = -i\{j_1(\sigma d)[Y_{11}(\Omega_{d_{12}}) + Y_{11}(\Omega_{d_{14}})] \\ + j_1(\sigma d\sqrt{2})Y_{11}(\Omega_{d_{13}})\},$$

where

$$Y_{11}(\Omega_{d_{12}}) + Y_{11}(\Omega_{d_{14}}) \\ = \frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2} \left\{ -\frac{d/\sqrt{2} + id/\sqrt{2}}{d} + \frac{d/\sqrt{2} + id/\sqrt{2}}{d} \right\} = i\left(\frac{3}{4\pi}\right)^{1/2}$$

and

$$Y_{11}(\Omega_{d_{13}}) = (i/2)(3/2\pi)^{1/2}.$$

This leads to

$$S_{11} = (3/4\pi)^{1/2}(j_1(\sigma d) + j_1(\sigma d\sqrt{2})/\sqrt{2}).$$

Some other elements are: $S_{1,-1} = S_{11}$; $S_{10} = S_{2,\pm 1} = S_{2,\pm 2} = 0$; $S_{20} = \frac{1}{4}(5/\pi)^{1/2}[2j_2(\sigma d) + j_2(\sigma d\sqrt{2})]$.