Solution by Recursion of the N -Body Electrostatic Schrödinger Equation

(atomic wavefunctions/hyperspherical expansions)

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ABSTRACT A generalized partial wave expansion of atomic wavefunctions has been shown to allow exact solution of the many-electron Schrödinger equation. This solution is constructed here by an algebraic recursion method, and several analytical properties of such wavefunctions are easily obtained. Eigenstates of the atom correspond to such solutions which satisfy certain boundary conditions for infinite extension of the system. A method of locating these states is presented.

Hyperspherical coordinates (1, 2) have proven useful to several theoretical investigations of exact N -body wavefunctions (3-7), but they appear to have been explicitly used only twice for actual calculations (8, 9). Elsewhere, I have described in detail the general application of these coordinates to the practical description of N -electron atoms (10). In this paper, I present a set of algebraic recursion relations for an infinite three-dimensional array of coefficients $A_{n,m}^{(\nu)}$, from which the exact wavefunction for any atom or ion can be determined.

The $3N$ -dimensional configuration $\mathbf{r}$ of the system is specified by the hyper-radius $r \equiv (r_1^2 + r_2^2 + \dots + r_N^2)^{1/2}$ and $3N - 1$ angles Ω . Fock (3) and others (4-6) have suggested an expansion of the spatial wavefunction in the form

$$\psi(\mathbf{r}) = \sum_{n=k}^{\infty} \sum_{m=0}^{[n/2]} a_{n,m}(\Omega) r^n \ln^m r, \quad [1]$$

where k is a nonnegative integer, and the functions $a_{n,m}$ are to be determined from the Schrödinger equation. This leads to a recursive set of differential equations

$$\begin{aligned} [\Lambda^2 - n(n + 3N - 2)]a_{n,m} &= (m + 2)(m + 1)a_{n,m+2} \\ &+ (m + 1)(2n + 3N - 2)a_{n,m+1} \\ &+ 2Ea_{n-2,m} - 2Wa_{n-1,m}. \end{aligned} \quad [2]$$

Here, Λ^2 is the Laplacian on the surface of a $3N$ -dimensional sphere, E is the energy, and W is the "angular" part of the total electrostatic potential energy $V(\mathbf{r}) = r^{-1}W(\Omega)$. The $a_{n,m}$ are obtained successively by solving this $(3N - 1)$ -dimensional differential equation for increasing n , and for decreasing m at fixed n —a two-dimensional triangular recursion. The boundary conditions are evident from Eq. 1:

$$a_{k-2,m} = a_{k-1,m} = 0 \text{ for any } m, \quad [3a]$$

$$a_{n,[n/2]+2} = a_{n,[n/2]+1} = 0 \text{ for fixed } n. \quad [3b]$$

In his original application of this approach to $^1\text{S He}$ (a special case with only two angles in Ω), Fock observed, "This process of solution may clearly be continued indefinitely, the only difficulties being of a computational nature" (3). Beyond $^1\text{S He}$, however, there are other difficulties. The dimensionality

of the equations increased with increasing N , it becomes impossible to separate the angle variables in the electron repulsions, and this method does not account for angular momentum, spin, or antisymmetry properties.

Our work (10) is complementary to this approach. We have studied the eigenfunctions of Λ^2 , which satisfy

$$\Lambda^2 S_{\mu}^{L,M}(\nu|\Omega) = \lambda_{\nu}(\lambda_{\nu} + 3N - 2)S_{\mu}^{L,M}(\nu|\Omega) \quad [4]$$

and are simultaneous eigenfunctions of L^2 and L_z . They are grouped according to their permutational invariants ν , with the members of each invariant subset indexed by μ ; they are complete in Ω . We expand the total electronic wavefunction for a specific ^{2S+1}L state in the form (11)

$$\Psi^{L,M,S,M_S}(\mathbf{r},\sigma) = \sum_{\kappa=1}^f \psi_{\kappa}^{L,M}(\mathbf{r}) \theta_{\kappa}^{S,M_S}(\sigma), \quad [5]$$

and follow with a partial wave expansion of the spatial functions

$$\psi_{\kappa}^{L,M}(\mathbf{r}) = \sum_{\nu} \mathcal{R}(\nu|r) S_{\kappa}^{L,M}(\nu|\Omega). \quad [6]$$

The functions θ_{κ}^{S,M_S} of the spin variables σ are basis functions for the spin state, while the angular functions are the specific linear combinations

$$S_{\kappa}^{L,M}(\nu|\Omega) = \sum_{\mu} C_{\mu,\kappa} S_{\mu}^{L,M}(\nu|\Omega) \quad [7]$$

constructed from each permutationally invariant subspace such that Ψ satisfies the Pauli principle.

The expansion in Eqs. 5 and 6 can be used in the Schrödinger equation to give a set of coupled differential equations that the radial functions must satisfy (10). We have examined the exact solution of the finite set of these equations which are obtained when the expansion in Eq. 6 is truncated to N_i terms (12). The results depend on the N_i constants λ_{ν} , which we assume are arranged in natural (ascending) order $\lambda_1 \leq \lambda_2 \leq \dots$. Generally, $\mathcal{R}(\nu|r)$ is a sum of terms of the form $A_{n,m}^{(\nu)} r^n \ln^m r$, where n starts at λ_1 and runs to infinity, and m starts at zero and is restricted to $m < \nu - 1$ for $\lambda_{\nu-1} \leq n < \lambda_{\nu}$. For n greater than the largest λ_{ν} , m is restricted to $m < N_i$. We clarify these restrictions by noting that $S_{\kappa}(\nu|\Omega)$ has the parity of λ_{ν} under inversion of all electrons, hence the set $\{\lambda_{\nu}\}$ for a given state will contain only even or odd integers. Thus, the spatial wavefunction has the expansion

$$\psi_{\kappa}^{L,M}(\mathbf{r}) = \sum_{\nu} \sum_{n=k}^{\infty} \sum_{m=0}^{m^*(n)} A_{n,m}^{(\nu)} r^n \ln^m r S_{\kappa}^{L,M}(\nu|\Omega), \quad [8]$$

where k is identified λ_1 , and $m^*(n) = [n/2] - d(n)$, where $d(n)$ is the number of even or odd integers less than n that

do not appear in $\{\lambda_\nu\}$. As N_t approaches infinity, $m^*(n)$ is the only restriction on m .

Eq. 8 is the expansion we want. Substitution into the Schrödinger equation, and use of the linear independence of the basis, gives a two-dimensional, algebraic recursion formula (see footnote*) for $A_{n,m}^{(\nu)}$:

$$\begin{aligned} (\lambda_\nu - n)(\lambda_\nu + n + 3N - 2)A_{n,m}^{(\nu)} \\ = (m + 2)(m + 1)A_{n,m+2}^{(\nu)} \\ + (m + 1)(2n + 3N - 2)A_{n,m+1}^{(\nu)} \\ + 2E A_{n-2,m}^{(\nu)} - 2\Sigma_\nu W_{\nu,\nu'} A_{n-1,m}^{(\nu')} \quad [9] \end{aligned}$$

where $W_{\nu,\nu'}$ is the matrix element of W between $S_\kappa(\nu|\Omega)$ and $S_\kappa(\nu'|\Omega)$, and is independent of κ . It is easily expressed in terms of Beta functions and $3 - j$ coefficients. Given the angular basis, it is now straightforward to compute the A coefficients: recur upwards in n from k ; for fixed n , recur downwards in m from m^* ; for fixed n and m , solve for all ν . The boundary conditions are

$$A_{k-2,m}^{(\nu)} = A_{k-1,m}^{(\nu)} = 0 \text{ for all } m \text{ and } \nu, \quad [10a]$$

$$A_{n,m+2}^{(\nu)} = A_{n,m+1}^{(\nu)} = 0 \text{ for fixed } n \text{ and all } \nu. \quad [10b]$$

It is essential to understand what happens when n is equal to one of the λ_ν , say $\lambda_\mu = l$. The equations for $A_{l,m}^{(\mu)}$ have a zero on the lhs for $\nu = \mu$, so they determine all these coefficients except $A_{l,m}^{(\mu)}$. The equations for $A_{l,m}^{(\mu)}$ then give all these coefficients, except the equation for $\nu = \mu$, which now determines $A_{l,m}^{(\mu)}$. Continuing, we see that all coefficients $A_{l,0}^{(\mu)}$ for $l = \lambda_\mu$ are not determined by Schrödinger's equation; they depend on the spatial boundary conditions.

To conclude the solution of the bound state problem requires E and $\{A\}$, the set of arbitrary coefficients, to be determined such that $\psi_\kappa(r) \rightarrow 0$ as $r \rightarrow \infty$. This determination can be made implicitly by use of the particular solution concept, which we describe for N_t finite. We can generate N_t linearly independent functions from Eq. 9 by using N_t linearly independent coefficient sets $\{A^{(\alpha)}\}$, which we choose to be the unit vectors in N_t -dimensional space. Select a value of E , and generate the N_t solution sets (see footnote†) $\{\mathcal{R}^{(\alpha)}(\nu|r), \nu = 1, 2, \dots, N_t\}$, $\alpha = 1, 2, \dots, N_t$. For a bound state, we require for each ν that

$$\mathcal{R}(\nu|r) = A_{\lambda_1,0}^{(1)}\mathcal{R}^{(1)}(\nu|r) + A_{\lambda_2,0}^{(2)}\mathcal{R}^{(2)}(\nu|r) + \dots \rightarrow 0 \quad [11]$$

as $r \rightarrow \infty$; thus, if E is an eigenvalue, the particular solutions become linearly dependent. We test our guess of E by forming the determinant of a matrix $R(E)$ with elements $R_{\alpha,\nu} = \mathcal{R}^{(\alpha)}(\nu|r_\infty)$ and r_∞ is some large value of r . For eigenenergies, $|R(E)| = 0$. Conceptually, we find the exact E as a limiting value of the E s determined by using successively larger N_t and r_∞ .

An alternative to this procedure is to identify $\mathcal{R}_\infty(\nu|r)$, the correct asymptotic form of $\mathcal{R}(\nu|r)$, remove it by writing $\mathcal{R}(\nu|r) = F(\nu|r)\mathcal{R}_\infty(\nu|r)$, and then quantize E by truncating an expansion of F .

Certain analytical properties of ψ may be examined without knowledge of E . To illustrate, we consider 1S He. In this case Ω contains the two angles $\eta = \tan^{-1}(r_1/r_2)$ and $\theta = \cos^{-1}$

$(\mathbf{r}_1 \cdot \mathbf{r}_2 / r_1 r_2)$. Fock (3) has obtained explicitly the coefficients $a_{0,0}$ and $a_{1,0}$, and White and Stillinger (7) have obtained part of $a_{2,1}$. The hyperspherical basis for this reduced problem has been given (7), and can be enumerated by two indices, $S(\nu|\Omega) = \Phi_{n,l}(\Omega)$, $n = 0, 1, 2, \dots$, and $l = 0, 1, \dots, n$. The antisymmetry requirement on the state restricts n and l to combinations satisfying $n - l = \text{even}$. Thus, we have the basis $\Phi_{0,0}, \Phi_{1,1}, \Phi_{2,0}, \dots$, and $\lambda_\nu = 2n = 0, 2, 4, \dots$. Since none of the even integers is missing in $\{\lambda_\nu\}$, we have $m^*(n) = [n/2]$, in agreement with Fock.

From Eq. 9 we deduce the results: $A_{0,0}^{(1)}$ is arbitrary and $A_{0,0}^{(\nu)} = 0$ for $\nu = 2, 3, \dots$; then $A_{1,0}^{(\nu)} = U_\nu A_{0,0}^{(1)}$ for all ν , with

$$U_\nu = -2[(\lambda_\nu - 1)(\lambda_\nu + 5)]^{-1}W_{\nu,1}. \quad [12]$$

For $n = 2$, there are two values of m . For $m = 1$, $A_{2,1}^{(2)}$ is not determined, but $A_{2,1}^{(\nu)} = 0$ for $\nu = 1, 3, 4, \dots$. From the $m = 0$ equation, $A_{2,0}^{(2)}$ is arbitrary, but $A_{2,1}^{(2)} = 1/4 Q_2 A_{0,0}^{(1)}$ and $A_{2,0}^{(\nu)} = -2[(\lambda_\nu - 2)(\lambda_\nu + 6)]^{-1}[\delta_{\nu,1}E - Q_\nu]A_{0,0}^{(1)}$ for $\nu = 1, 3, 4, \dots$, where

$$Q_\nu = \Sigma_\nu W_{\nu,\nu'} U_{\nu'}. \quad [13]$$

Setting $A_{0,0}^{(1)} \equiv \pi^{1/2}$ and omitting the subscript κ , we obtain

$$\psi(\mathbf{r}) = 1 + r \Sigma_\nu \pi^{1/2} U_\nu S(\nu|\Omega) + \frac{\pi^{1/2}}{4} Q_2 r^2 \ln r S(2|\Omega) + O(r^2) \quad [14]$$

It may be verified that $\pi^{1/2} U_\nu$ is just the projection of $-Z(r_1 + r_2) + 1/2 r_{12}$ onto $S(\nu|\Omega)$. Also, due to the completeness of the angular basis, we can identify $\pi^{1/2} Q_\nu$ as the projection onto $S(\nu|\Omega)$ of

$$1/2 - Z(r_1 + r_2) \left(\frac{1}{r_{12}} + \frac{r_{12}}{2r_1 r_2} \right) + Z^2 \left(2 + \frac{r^2}{r_1 r_2} \right).$$

Thus, we get

$$\begin{aligned} \psi(\mathbf{r}) = 1 - Zr_1 - Zr_2 + 1/2 r_{12} \\ + 1/2 Q_2 r_1 r_2 \cos \theta \ln(r_1^2 + r_2^2) + \dots, \quad [15] \end{aligned}$$

which agrees with previous results except for the coefficient of the logarithmic term. The difference arises because White and Stillinger (7) used a first-order perturbation theory. Since the function $S(2|\Omega)$ contains $P_1(\cos \theta)$, the spherical terms in Q_2 do not contribute and the correct Q_2 is strictly proportional to Z ; White and Stillinger's coefficient contain terms in both Z and Z^2 .

We draw attention in Eq. 14 to the coefficient of r which gives the cusp behavior. An infinite series is necessary for this due to the nature of basis. We have solved the angular momentum, spin, and antisymmetry problems by imposing appropriate restrictions on the eigenfunctions of the kinetic energy operator on the unit hypersphere to generate the "symmetry-adapted" basis $S(\nu|\Omega)$. But the angular potential $W(\Omega)$ has many singularities on this same hypersphere, and these had no influence in shaping that basis, hence the infinite series to describe behavior around these singularities. This appears to be general: potential singularities on the hypersphere of finite radius slow convergence of the hyperspherical expansion to the exact result (private communication, J. E. Kilpatrick).

The case of 3S Li shows another discrepancy between our results and previous work. Demkov and Ermolaev (4) concluded that k , the lowest power of r , is given by the sum of the

* Except for the change in n and m summation limits, this is just what one would get by expanding the Fock coefficients $a_{n,m}$ in our basis $S(\nu|\Omega)$ with coefficients $A_{n,m}^{(\nu)}$.

† These are just the particular solutions in ref. 12.

electrons' azimuthal quantum numbers, as obtained from approximate independent-particle wavefunctions. Thus, for the configuration $(1s)^2 (2s)$, we find k to be zero. This is incorrect. In constructing the hyperspherical basis for this state, we find the smallest allowed value of λ is 2. The $\lambda = 0$ case is ruled out by antisymmetry requirements.

In summary, I have presented a simple algebraic recursion method for obtaining the wavefunction for any atomic state.

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