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Variational trial functions in quantum theory

I. Bound states

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Abstract. We give a method of calculating variational trial functions in quantum theory. Applications are made to the discrete spectra of some simple one and two particle systems.

1. Introduction

Variational techniques have proved to be one of the most powerful methods in quantum mechanics. The biggest drawback in their application is the choice of a trial function: these functions are arbitrary apart from being integrable and having to satisfy boundary conditions in some methods. Here we propose a method which takes some account of the field in the functional form of the trial function and is similar to the variation-iteration method (see Morse and Feshbach 1953 p 1137–46, McEachran *et al* 1965, Kraidy and Fraser 1966, Bazley and Fox 1961 and Robinson 1969).

In principle it is possible to consider the complex spectrum with the discrete and continuous spectra as special cases. However, when variational methods are used as a means of calculating wavefunctions as well as energy eigenvalues or phase shifts, then it is more convenient in computations to consider these cases separately. The integrals involved in the measurement of dynamical variables or transitions of systems, can be very sensitive to the accuracy of the wavefunctions. In this paper, referred to as I, we give a general account of the method and its application to the calculation of bound states, and in a second paper, referred to as II, we consider applications to the continuous spectrum. As the main purpose of these papers is to discuss the usefulness of the proposed method and assess its accuracy, we restrict all applications to one and two electron systems, where the solutions are already known.

2. The method for one particle systems

Consider a particle of energy E and orbital angular momentum l moving in the central field potential $U(r)$; generalization to more complicated systems is given later. We have to solve the Schrödinger equation (in atomic units)

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) + E \right) f_l(E|r) = 0 \quad (1)$$

where $f_l(E|r)$ satisfies the boundary conditions

$$\begin{aligned}
 f_l(E|0) &= 0 \\
 f_l(E|r) &\underset{r \rightarrow \infty}{\sim} \frac{N}{k} \sin(kr - \frac{1}{2}l\pi + \eta_l) \text{ for continuous states } (E = k^2 > 0) \\
 f_l(E|r) &\underset{r \rightarrow \infty}{\sim} N' e^{-Kr} \text{ for discrete states } (E = -K^2 < 0)
 \end{aligned}
 \tag{2}$$

and η_l is the scattering phase shift and N and N' are normalizing constants. Alternatively, we can use the integral equation

$$f_l(E|r) = u_l(E|r) + \int_0^\infty G_l(E_0|x, r) (-U(x) + E - E_0) f_l(E|x) dx
 \tag{3}$$

to calculate $f_l(E|r)$, where $E \leq E_0$ for $E < 0^\dagger$ and $E = E_0$ for $E \geq 0$. The function $u_l(E|r)$ and the free particle Green function $G_l(E|x, r)$ are given by

$$\begin{aligned}
 u_l(k^2|r) &= \frac{N}{k} j_l(kr) \cos \eta_l \\
 u_l(-K^2|r) &= 0 \\
 G_l(k^2|x, r) &= \frac{1}{k} j_l(kx) n_l(kr) \quad 0 \leq x \leq r \\
 &= \frac{1}{k} j_l(kr) n_l(kx) \quad r < x < \infty \\
 G_l(-K^2|x, r) &= \frac{1}{K} j_l(iKx) h_l^*(iKr) \quad 0 \leq x \leq r \\
 &= \frac{1}{K} j_l(iKr) h_l^*(iKx) \quad r < x < \infty
 \end{aligned}
 \tag{5}$$

and the functions $j_l(z)$, $n_l(z)$ and $h_l(z)$ can be expressed in terms of Bessel functions

$$\begin{aligned}
 j_l(z) &= (\frac{1}{2}\pi z)^{1/2} J_{l+\frac{1}{2}}(z) \\
 n_l(z) &= (-1)^l (\frac{1}{2}\pi z)^{1/2} J_{-l-\frac{1}{2}}(z) \\
 h_l(z) &= j_l(z) + in_l(z).
 \end{aligned}
 \tag{6}$$

The expression (3) is more general than the usual one that appears in the literature and $E \neq E_0$ is possible in the case of the discrete spectrum. We can use an iteration procedure to solve equation (3) and this approach has the advantage that convergence can be obtained for a wide variety of initial functions; although there is no guarantee that the iterations will converge. For the continuous spectrum the Born procedure uses plane waves for its initial functions, Saraph and Seaton (1962) and Saraph (1963) incorporate iteration and variational methods to speed up convergence of the iterated numerical solution of coupled integro-differential equations arising in scattering theory,

[†] For example in the case $E < 0$, $l = 0$ from equation (3) $f_0(-K^2|r)$ behaves asymptotically as

$$f_0(-K^2|r) \underset{r \rightarrow \infty}{\sim} \frac{\exp(-K_0 r)}{2K_0} \int_0^\infty (e^{K_0 x} - e^{-K_0 x})(K_0^2 - K^2 - U(x)) f_0(-K^2|x) dx$$

the integral only converges if $K \geq K_0$, that is, $E_0 \geq E$.

and McEachran *et al* (1965) and Kraidy and Fraser (1966) use an iteration procedure and variational methods; their technique is similar to that given here and will be discussed more fully in II.

We use equation (3) to define the trial functions f_i^1 , and for convenience in discussion, we shall divide them into two types: type 1

$$f_i^1(E|r) = u_i(E|r) + \int_0^\infty G_i(E_0|x, r)(-U(x) + E - E_0)\phi(x) dx \tag{7}$$

and type 2, the iterated functions

$$f_i^{(n)}(E|r) = u_i(E|r) + \int_0^\infty G_i(E_0|x, r)(-U(x) + E - E_0)f_i^{(n-1)}(E|x) dx \tag{8}$$

$n \geq 1$

where $\phi(x)$ and $f_i^{(0)}(E|x)$ are suitably chosen so that the integrals (7) and (8) exist and we assume that they depend on a set of m parameters $c_i (i = 1, 2, \dots, m)$. The trial functions (7) and (8) take some account of $U(r)$ in their functional form and it is to be expected that calculations with (8) will increase in accuracy the more iterations taken.

3. The discrete spectrum

For the discrete spectrum the energy E is unknown. We can, however, compute the integrals involved in equation (3), numerically if necessary, once we assign a value to E_0 . For the exact wavefunction, the integral (3) will converge only if $E_0 \geq E$; with approximate wavefunctions this restriction can be avoided.

The trial functions of type 1 can be subdivided into type 1a

$$f_i^1(E|r) = \int_0^\infty G_i(E_0|x, r)(-U(x) - E_0)\phi(x) dx + \lambda \int_0^\infty G_i(E_0|x, r)\phi(x) dx \tag{9}$$

or type 1b, in the special case $E = E_0 = -K^2$

$$f_i^1(E|r) = - \int_0^\infty G_i(-K^2|x, r)U(x)\phi(x) dx \tag{10}$$

where we have written λ for E in equation (9), and we shall refer to them as type 1a and type 1b as indicated.

Using the Rayleigh-Ritz method, trial functions are substituted in the variational integral

$$E^1 = - \left\{ \int_0^\infty f_i^1(E|r) \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) \right) f_i^1(E|r) dr \right\} \left\{ \int_0^\infty \{f_i^1(E|r)\}^2 dr \right\}^{-1} \tag{11}$$

and the parameters are calculated in the usual way. However, the functions (9) and (10) are not suitable as λ and K are functions of the energy, as yet undetermined. We adopted the procedure of treating λ or K as a parameter; thus the values of λ and $-K^2$ in calculations will not necessarily be equal to the energy.

Since $\phi(x)$ depends on the parameters $c_i (i = 1, \dots, m)$, we can calculate their values and that of λ or K from the equations

$$\begin{aligned} \frac{\partial E^1}{\partial c_i} &= 0 & i = 1, \dots, m \\ \frac{\partial E^1}{\partial \lambda} &= 0 & \text{or} & \frac{\partial E^1}{\partial K} = 0. \end{aligned} \quad (12)$$

Trial functions of type 2 can be used in a similar way; the n th iterated function corresponding to (9) will be an n th order polynomial in λ and the function corresponding to (10), an n dimensional integral. Calculations with such trial functions will be of practical importance if the integrals are relatively simple. It is usually possible to obtain an improvement in accuracy with type 1 functions by making $\phi(x)$ a more sophisticated function involving more parameters. Because of the practical difficulties involved in using type 2 trial functions the calculations discussed in §§ 4 and 5 are confined to type 1 functions.

4. Applications to some one particle systems

To illustrate the method we have applied types 1a and 1b trial functions to the central field potentials

(i) square well

$$\begin{aligned} U(r) &= -U_0 & 0 \leq r \leq r_0 \\ &= 0 & r_0 < r < \infty \end{aligned} \quad (13)$$

(ii) exponential potential

$$U(r) = -U_0 \exp(-r/r_0) \quad (14)$$

(iii) Coulomb potential

$$U(r) = -2Z/r \quad (15)$$

where U_0 , r_0 and Z are constants. We have confined our applications to the case $l = 0$ and the ground state energy eigenvalue. The one particle Green function for this case and $E_0 < 0$ is given by

$$\begin{aligned} G_0(-K^2|x, r) &= \frac{1}{K} \sinh Kx e^{-Kr} & 0 \leq x \leq r \\ &= \frac{1}{K} \sinh Kr e^{-Kx} & r < x < \infty. \end{aligned} \quad (16)$$

Applications to excited states can be made in the usual way, providing the excited state trial functions are made orthogonal to those of the ground state.

Calculations for the square well and exponential potential can be simplified by making the change of variable $r' = r/r_0$ and all cases are covered by varying $U'_0 = U_0 r_0^2$ and scaling the energy (ie dividing by r_0^2). This is equivalent to putting $r_0 = 1$ and $U_0 = U'_0$ in equations (13) and (14); this holds for exact and variational calculations, including those with trial functions (9) and (10).

A similar simplification is possible for the Coulomb potential (15); using the variable $r' = r/Z$, all cases are covered by $Z = 1$ and scaling the energy (ie multiplying by Z^2).

Variational methods are also an important means of calculating wavefunctions. We give tables of the ground state energy and expectation values of $\langle r^p \rangle$ ($p = -2, -1, 1, 2$). We also compare graphically exact and variational wavefunctions.

For the square well and exponential potentials, we have used the function

$$\phi(x) = x e^{-\alpha x} \tag{17}$$

α being a number fixed arbitrarily. The trial functions corresponding to (9) and (10) are very simple one parameter functions, with λ or K as parameters. Results for the trial function

$$f_0^1(r) = r e^{-cr} \tag{18}$$

Table 1. Binding energy and expectation values for the square well potential

(a) $U_0 = 4, r_0 = 1$										
Binding energy										
Function		Type 1a				Type 1b		ϕ	Numerical	
x	$(-E_0)^{1/2}$	0.25	$\sqrt{0.407}$	0.75	1.25	1.75				
	0.7		0.399	0.407	0.407	0.398	0.384	0.407		
1.0		0.406	0.407	0.407	0.405	0.403	0.407			
1.077		0.405	0.406	0.406	0.405	0.403	0.406	0.300	0.407	
1.3		0.397	0.405	0.404	0.401	0.398	0.405			
1.6		0.379	0.400	0.400	0.391	0.379	0.400			
Expectation values $\langle r^p \rangle$										
Function		Type 1a				Type 1b		ϕ	Numerical	
p	x	$(-E_0)^{1/2}$	0.25	$\sqrt{0.407}$	0.75	1.25	1.75			
			0.25	$\sqrt{0.407}$	0.75	1.25	1.75			
-2	0.7		2.02	2.18	2.20	2.17	2.08	2.17		
	1.0		2.25	2.24	2.25	2.25	2.25	2.24		
	1.077		2.28	2.26	2.26	2.28	2.29	2.25	2.32	2.20
	1.3		2.33	2.29	2.30	2.35	2.41	2.29		
	1.6		2.31	2.33	2.35	2.45	2.56	2.33		
-1	0.7		1.09	1.13	1.13	1.11	1.07	1.13		
	1.0		1.14	1.14	1.14	1.14	1.13	1.14		
	1.077		1.15	1.14	1.14	1.15	1.15	1.14	1.08	1.14
	1.3		1.15	1.15	1.15	1.17	1.18	1.15		
	1.6		1.12	1.15	1.16	1.19	1.22	1.15		
1	0.7		1.32	1.28	1.30	1.40	1.51	1.28		
	1.0		1.29	1.28	1.28	1.29	1.31	1.28		
	1.077		1.31	1.29	1.28	1.28	1.28	1.29	1.39	1.28
	1.3		1.40	1.29	1.28	1.23	1.21	1.29		
	1.6		1.57	1.30	1.27	1.19	1.15	1.31		
2	0.7		2.32	2.29	2.40	3.01	3.54	2.28		
	1.0		2.40	2.32	2.31	2.34	2.40	2.32		
	1.077		2.59	2.33	2.30	2.25	2.25	2.33	2.59	2.32
	1.3		3.38	2.36	2.26	2.03	1.94	2.37		
	1.6		4.64	2.40	2.23	1.86	1.70	2.45		

Table 1—continued

(b) $U_0 = 8, r_0 = 1$								
Binding energy								
Function		Type 1a			Type 1b	ϕ	Numerical	
α	$(-E_0)^{1/2}$	0.75	1.25	$\sqrt{3.02}$	1.75	2.25		
1.3		2.94	3.00	3.01	3.01	3.01		
1.6		2.99	3.01	3.00	3.00	2.99		
1.631		2.99	3.01	3.00	3.00	2.99	3.00	
1.9		3.00	2.99	2.98	2.98	2.97	2.99	
2.2		2.98	2.97	2.95	2.95	2.93	2.96	
Expectation values $\langle r^p \rangle$								
Function		Type 1a			Type 1b	ϕ	Numerical	
p	α	$(-E_0)^{1/2}$	0.75	1.25	$\sqrt{3.02}$	1.75	2.25	
-2	1.3		3.76	4.04	4.21	4.21	4.31	4.21
	1.6		4.09	4.28	4.41	4.41	4.51	4.37
	1.631		4.12	4.31	4.43	4.43	4.53	4.41
	1.9		4.38	4.50	4.61	4.61	4.72	4.54
	2.2		4.63	4.70	4.80	4.81	4.94	4.69
-1	1.3		1.54	1.60	1.64	1.64	1.65	1.64
	1.6		1.61	1.64	1.66	1.66	1.68	1.66
	1.631		1.61	1.65	1.67	1.67	1.68	1.66
	1.9		1.66	1.68	1.69	1.69	1.70	1.68
	2.2		1.69	1.70	1.71	1.71	1.73	1.69
1	1.3		0.85	0.80	0.79	0.79	0.79	0.79
	1.6		0.80	0.78	0.78	0.78	0.78	0.78
	1.631		0.80	0.78	0.78	0.78	0.78	0.78
	1.9		0.78	0.78	0.78	0.78	0.78	0.78
	2.2		0.78	0.78	0.78	0.78	0.77	0.78
2	1.3		0.92	0.77	0.74	0.74	0.77	0.75
	1.6		0.78	0.74	0.74	0.74	0.76	0.75
	1.631		0.77	0.74	0.74	0.74	0.76	0.75
	1.9		0.74	0.74	0.74	0.74	0.75	0.75
	2.2		0.74	0.74	0.75	0.75	0.75	0.76

where c is a parameter, have been included for the purposes of comparison. These results give some indication of how well the functional form of $\phi(x)$ agrees with the exact function. Calculations with type 1a and 1b trial functions and $\alpha = c$ (the variational parameter calculated with equation (18)) provide a good measure of any improvements given by the method.

In table 1(a and b) results are given for the square well potential. The trial function defined by equation (17) and equation (9) or (10) gives more accurate energy values than (18). That is, errors of over 20% are reduced to between 0.1 and 3% depending on the value chosen for α and E_0 . For the exponential potential, equation (18) is a much better approximation to the wavefunction. However, as can be seen in table 2(a and b) type 1 functions give improved results.

Table 2—continued

(b) $U_0 = 8, r_0 = 1$									
Binding energy									
Function		Type 1a				Type 1b	ϕ	Numerical	
α	$(-E_0)^{1/2}$	0.75	$\sqrt{1.46}$	1.25	1.75	2.25			
	0.5		1.31	1.40	1.41	1.45	1.46	1.45	
0.8		1.42	1.45	1.45	1.46	1.45	1.46		
1.104		1.45	1.45	1.46	1.45	1.44	1.45	1.39	1.46
1.4		1.45	1.45	1.45	1.45	1.45	1.45		
1.7		1.43	1.45	1.45	1.46	1.46	1.44		
Expectation values $\langle r^p \rangle$									
Function		Type 1a				Type 1b	ϕ	Numerical	
p	α	$(-E_0)^{1/2}$	0.75	$\sqrt{1.46}$	1.25	1.75	2.25		
			0.75	$\sqrt{1.46}$	1.25	1.75	2.25		
-2	0.5		1.25	1.58	1.61	1.89	2.11	2.13	
	0.8		1.71	1.98	2.00	2.19	2.30	2.13	
	1.104		2.08	2.18	2.18	2.22	2.22	2.17	2.44
	1.4		2.27	2.20	2.20	2.16	2.13	2.23	
	1.7		2.29	2.16	2.15	2.10	2.09	2.32	
-1	0.5		0.85	0.96	0.97	1.05	1.10	1.11	
	0.8		1.00	1.07	1.08	1.12	1.14	1.11	
	1.104		1.10	1.12	1.12	1.12	1.12	1.11	1.10
	1.4		1.13	1.12	1.12	1.11	1.10	1.12	
	1.7		1.12	1.10	1.10	1.10	1.11	1.14	
1	0.5		1.64	1.42	1.41	1.30	1.25	1.25	
	0.8		1.37	1.27	1.26	1.24	1.24	1.24	
	1.104		1.25	1.24	1.24	1.26	1.28	1.25	1.36
	1.4		1.25	1.26	1.26	1.27	1.27	1.25	
	1.7		1.29	1.28	1.27	1.25	1.23	1.26	
2	0.5		3.81	2.62	2.56	2.09	1.96	1.99	
	0.8		2.40	1.99	1.98	1.94	2.03	1.94	
	1.104		1.96	1.95	1.96	2.04	2.14	1.98	2.46
	1.4		2.02	2.05	2.05	2.06	2.06	2.03	
	1.7		2.24	2.09	2.08	1.96	1.88	2.10	

These calculations are relatively insensitive to α and E_0 and the 25% error in the energy calculated with (20) was reduced to a few per cent in most cases.

Graphical comparison of the exact and typical variational functions for these potentials is given in figures 1, 2 and 3. For the square well and exponential potentials, on the scale used in the diagrams, it is not possible to differentiate between the exact and type 1a functions, and for the Coulomb potential it is not possible to differentiate between the exact and type 1b functions.

For all the potentials we have included the case of α in (17) or (19) equal to the variational value c in (18) or (20), and without exception there is considerable improvement in accuracy using type 1a and 1b trial functions.

Table 3. Binding energy and expectation values for the Coulomb potential, $Z = 1$

Binding energy		Type 1a					Type 1b	ϕ	Numerical
Function									
$(-E_0)^{1/2}$									
α		0.6	1.0	1.4	2.2	3.0			
1.2		0.938	0.948	0.957	0.969	0.978	0.979		
1.5		0.967	0.965	0.964	0.965	0.967	0.964		
1.6		0.973	0.968	0.965	0.961	0.960	0.965	0.750	1.00
2.0		0.985	0.973	0.956	0.928	0.909	0.976		
2.4		0.989	0.969	0.934	0.871	0.825	0.985		
Expectation values $\langle r^p \rangle$		Type 1a					Type 1b	ϕ	Numerical
Function									
$(-E_0)^{1/2}$									
p	α	0.6	1.0	1.4	2.2	3.0			
	1.2	1.22	1.33	1.43	1.57	1.66	1.98		
	1.5	1.48	1.53	1.59	1.70	1.78	1.61		
-2	1.6	1.54	1.58	1.64	1.74	1.82	1.57	0.75	2.00
	2.0	1.71	1.73	1.80	1.93	2.05	1.58		
	2.4	1.79	1.86	1.96	2.16	2.32	1.68		
	1.2	0.85	0.88	0.91	0.95	0.97	1.05		
	1.5	0.92	0.94	0.96	0.99	1.01	0.96		
-1	1.6	0.94	0.95	0.97	1.01	1.03	0.95	0.75	1.00
	2.0	0.97	0.99	1.02	1.07	1.11	0.95		
	2.4	0.98	1.03	1.08	1.15	1.20	0.96		
	1.2	1.60	1.53	1.50	1.46	1.45	1.36		
	1.5	1.51	1.47	1.44	1.39	1.37	1.43		
1	1.6	1.50	1.45	1.42	1.37	1.34	1.45	1.67	1.50
	2.0	1.51	1.41	1.34	1.26	1.21	1.49		
	2.4	1.52	1.35	1.26	1.16	1.10	1.50		
	1.2	3.17	2.92	2.80	2.72	2.70	2.38		
	1.5	2.91	2.73	2.60	2.45	2.38	2.57		
2	1.6	2.92	2.69	2.53	2.35	2.26	2.65	3.33	3.00
	2.0	3.07	2.53	2.25	1.96	1.82	2.85		
	2.4	3.18	2.35	1.99	1.65	1.48	3.00		

5. Two particle systems

We can in principle generalize the method described in § 2 to systems of two or more particles, however, certain practical difficulties are encountered. For example, for two electron helium-like systems of nuclear charge Z , the Schrödinger equation (in atomic units) is

$$\left(\nabla_1^2 + \nabla_2^2 + \frac{2Z}{r_1} + \frac{2Z}{r_2} - \frac{2}{r_{12}} + E \right) \psi(r_1, r_2) = 0 \quad (21)$$

r_1 and r_2 being the position vectors of the two electrons and $r_{12} = |r_1 - r_2|$. The two

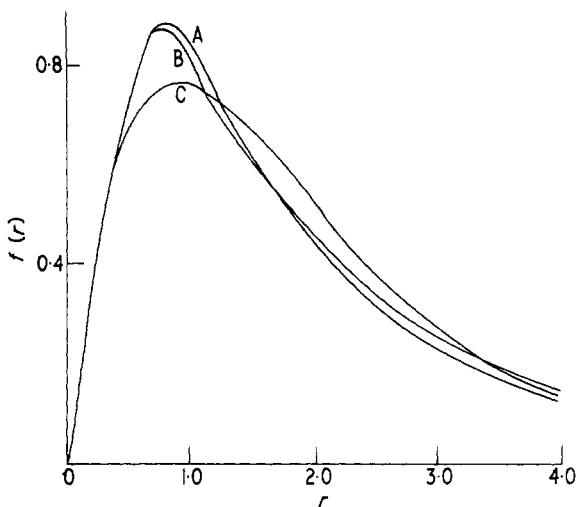


Figure 1. Radial wavefunction for the square well potential $U_0 = 4$. A exact solution, type 1b ($\alpha = 1.0$); B type 1a ($\alpha = 1.0, (-E_0)^{1/2} = 1.75$); C ϕ .

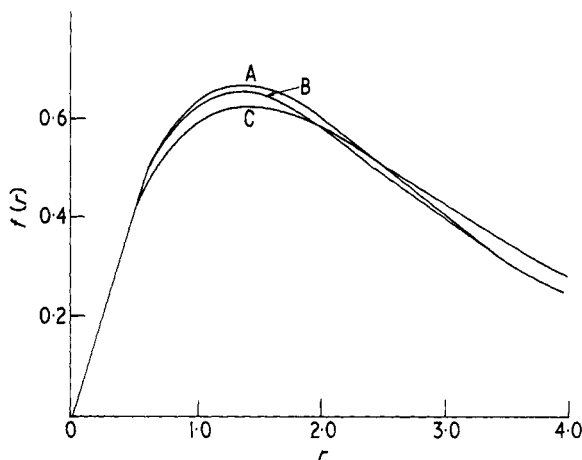


Figure 2. Radial wavefunction for the exponential potential $U_0 = 4$. A exact solution, type 1b ($\alpha = 0.5$); B type 1a ($\alpha = 0.5, (-E_0)^{1/2} = 1.25$); C ϕ .

particle Green function (both particles free) corresponding to equations (5) is a solution of the differential equation

$$(\nabla_1^2 + \nabla_2^2 + E_0)G(E_0|r_1, r_2; r'_1, r'_2) = -\delta(r_1 - r'_1)\delta(r_2 - r'_2). \tag{22}$$

The integral equation corresponding to the two particle system and bound states is

$$\psi(r_1, r_2) = \int G(E_0|r_1, r_2; r'_1, r'_2) \left(E - E_0 + \frac{2Z}{r'_1} + \frac{2Z}{r'_2} - \frac{2}{r'_{12}} \right) \psi(r'_1, r'_2) dr'_1 dr'_2 \tag{23}$$

for $E_0 \geq E$.

If we consider the ground state of such systems, the total orbital angular momentum is zero and the Green function can be expressed in terms of hyperspherical coordinates.

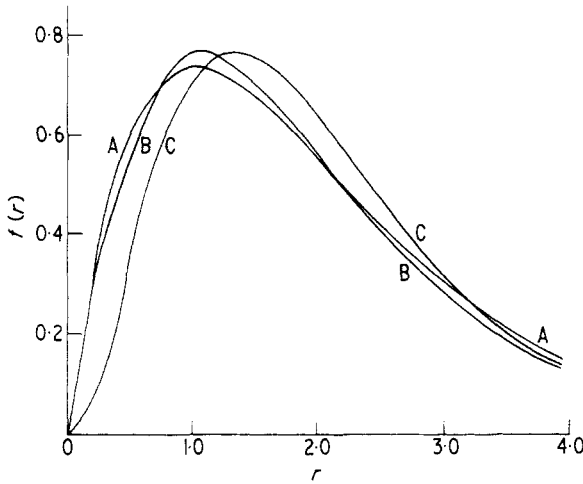


Figure 3. Radial wavefunction for the hydrogen atom. A exact solution, type 1a ($\alpha = 2.0$, $(-E_0)^{1/2} = 0.6$); B type 1b ($\alpha = 2.0$); C ϕ .

Morse and Feshbach (1953 p 1732 equation (12.3.92)) give a very complicated expression for the two particle Green function in terms of Jacobi polynomials, Bessel and Hankel functions and calculations with such expressions become quite impractical without some simplifications and we have not made use of their results here.

However, it is possible to simplify calculations by working in terms of one particle Green functions. For example, we can expand the wavefunction in the form

$$\psi(r_1, r_2) = \left(\frac{Z^3}{2\pi}\right)^{1/2} \{ \exp(-Zr_1)f(r_2) + \exp(-Zr_2)f(r_1) \}. \tag{24}$$

The resulting equation for $f(r)$ is

$$\left(\frac{d^2}{dr^2} - U(r) - \epsilon^2 \right) f(r) = 2P(r) \left(r^{-1} \int_0^r P(x)f(x) dx + \int_r^\infty P(x)f(x)x^{-1} dx - \frac{1}{2}(Z^2 - \epsilon^2) \int_0^\infty P(x)f(x) dx \right) \tag{25}$$

where

$$U(r) = \frac{-2(Z-1)}{r} - 2 \left(Z + \frac{1}{r} \right) \exp(-2Zr) \tag{26}$$

$$P(r) = 2(Z)^{3/2}r \exp(-Zr)$$

and

$$E = -Z^2 - \epsilon^2.$$

The derivation of equation (25) for continuum states and $Z = 1$ can be found in numerous texts for example Bransden *et al* (1958).

The type 1a trial functions for this system are given by

$$f^i(r) = \int_0^\infty G_0(-\epsilon_0^2|x, r) \left\{ (\lambda + \epsilon_0^2 - U(x))\phi(x) - 2P(x) \left(x^{-1} \int_0^x P(x')\phi(x') dx' + \int_x^\infty P(x')\phi(x')x'^{-1} dx' - \frac{1}{2}(Z^2 + \lambda) \int_0^\infty P(x')\phi(x') dx' \right) \right\} dx \quad (27)$$

and type 1b functions can be obtained from (27) by putting $\lambda = -\epsilon_0^2 = K^2$. Results for $H^- (Z = 1)$ and $He (Z = 2)$ with

$$\phi(x) = x e^{-\alpha x} \quad (28)$$

are given in table 4. We also give the value of ϵ^2 computed from the numerical solution of (25), this corresponds to the most accurate value possible with a wavefunction of the form (24). As in the one particle calculations comparison with the trial function

$$f^i(r) = r e^{-\alpha r} \quad (29)$$

are also given in table 4. This trial function is more accurate for H^- than He, although type 1a and type 1b functions give more accurate results choosing α and ϵ_0 suitably.

Results for alternative expansions, the Hartree-Fock type (see Roothaan and Weiss 1960)

$$\psi(r_1, r_2) = F(r_1)F(r_2) \quad (30)$$

and the Hylleraas type

$$\psi(r_1, r_2) = F(r_1, r_2, r_{12}) \quad (31)$$

Table 4. Binding energy for helium-like systems

Z = 1										
Function	Type 1a					Type 1b	ϕ	HF	Pekeris	Numerical
α	$(Z^2 - E_0)^{1/2}$									
	0.05	0.15	$\sqrt{0.027}$	0.25	0.35					
0.1	1.023	1.026	1.026	1.025	1.024	1.026				
0.279	1.026	1.026	1.026	1.026	1.026	1.026				
0.3	1.026	1.026	1.026	1.026	1.026	1.026	1.025	0.976	1.056	1.027
0.5	1.021	1.026	1.026	1.026	1.023	1.026				
0.7	1.016	1.026	1.027	1.024	1.017	1.025				
Z = 2										
Function	Type 1a					Type 1b	ϕ	HF	Pekeris	Numerical
α	$(Z^2 - E_0)^{1/2}$									
	0.7	1.1	$\sqrt{1.745}$	1.5	1.9					
1.0	5.727	5.741	5.744	5.745	5.734	5.744				
1.286	5.744	5.744	5.744	5.744	5.744	5.744				
1.4	5.744	5.745	5.744	5.743	5.741	5.744	5.735	5.723	5.807	5.745
1.8	5.734	5.744	5.741	5.736	5.721	5.744				
2.2	5.728	5.743	5.735	5.726	5.700	5.744				

are also given in table 4. The greatest accuracy has been obtained by Pekeris (1958), however, the expansion (24) is an improvement on expansions of type (30), especially for H^- , where the attachment energy computed by the Hartree–Fock expansion is negative.

6. Conclusions

As with any method in mathematical physics, in assessing its usefulness, one has to weigh the obvious disadvantage in this case of calculating integrals to define trial functions, against the obvious improvements in accuracy particularly for the wavefunctions. It appears in practice that computations for bound states with type 1a functions are easier to handle than type 1b. A reliable guide to the constant E_0 is to choose the computed value for E . Applications to the continuous spectrum of similar systems are given in paper II.

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