Radial correlation in atoms

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Abstract. A method is described to calculate correlation energy in atoms. The total wavefunction of an n-electron system is expressed as a linear combination of products of n one-electron basis orbitals. This function gives a correlated description of the system. Under suitable restrictions it reduces to DODS and to split-shell description of closed-shell atoms or molecules. Energies of He atom, He-like ions and also of H^- ion have been calculated including radial correlation only. The calculated electron affinity of H is better than earlier split-shell calculations. The result for He shows that the energy limit for radial correlation has been attained. For the other 2-electron ions radial correlation alone explains about one-third of the total correlation.

1. Introduction

The purpose of this paper is to demonstrate a simple and straightforward way of calculating the energy correction due to radial correlations in an atom.

The practice of describing the state of a system of interacting fermions by anti-symmetrised product of one-particle functions has proved reasonably successfull for many investigations. Consequently the Hartree-Fock (HF) method has attained immense popularity for calculations in the field of atomic and nuclear structures (*see* for example, Hartree 1957, Kelson and Levinson 1964). However, such a description of many-particle systems has its limitation. It is manifested in the small but significant difference between calculated and observed energies. This is the correlation energy and is defined to be

$$E_{\text{corr}} = E_{\text{NR}} - E_{\text{HF}} \tag{1}$$

where E_{NR} is the total energy of the system in the non-relativistic approximation and E_{HF} is that calculated in the HF model (Löwdin 1959).

Various approaches, like configuration interaction (CI) (Slater 1960), Hylleraas-type expansion (using the inter-particle coordinates explicitly, *see* for example, Hylleraas 1929), and many body perturbation theory (MBPT) (Kelley 1969), have been developed to account for this difference in the energy value. A common feature of all these procedures is an order of magnitude increase in labour and complications in numerical computation over the conventional HF calculation.

The present method attempts to incorporate the dominant character of an interacting system, while retaining the mathematical simplicity of working on a single-particle basis set.

Our attitude may be described in simple terms by the following consideration. In principle, the state of a particle in a potential may be described by a linear combination of a complete set of functions. In practice, for bound states, a finite set of basis may be used to provide a reasonably adequate representation by making judicious choice of such basis functions. The Slater-type orbitals have proved successful in atomic calculations, while for molecules the LCAO's are extensively used. For nuclei different functions including the harmonic oscillator eigenfunctions are taken as is convenient for various investigations (*see* for example, Talmi 1952, Elliott 1958). In CI and MBPT calculations the starting requirement is the complete set of eigenstates of a suitable model Hamiltonian.

Now, if the set of basis orbitals X_k (*i*) span the one-particle space for the particle *i*, then the product space of *n* particles will be spanned by *n*-electron products of the form

$$g_a (1, 2, \ldots n) = X_k (1) X_l (2) \ldots X_p (n) \tag{2}$$

An arbitrary *n*-particle function may then be expressed as

$$\psi_{\text{corr}} (1, 2, \ldots n) = \sum_a c_a g_a. \tag{3}$$

Suitable constraints amongst the coefficients *c* need be imposed to ensure indistinguishability of similar particles, as also to make the function an eigenstate of L^2, L_z, S^2 and S_z in case of atoms or of S^2 and S_z for molecules. Further constraints are required if one wishes to factorise the composite function ψ_{corr} into products of single particle orbitals with real coefficients. If these additional constraints are not imposed, complex amplitudes are sometimes obtained implying different phase relations between the *X*'s. Otherwise, the function ψ_{corr} may be looked upon as a linear combination of determinants as appears in a CI description. Further, the function ψ_{corr} is more general and flexible than a DODS (different 'orbital' for different 'spin') (Löwdin 1964) or a split-shell representation (Harris and Pohl 1965) for closed shell systems.

Thus ψ_{corr} can give a correlated description of the *n*-particle system. It has the advantage that all basic integrals will be over single-particle functions. The conventional integrals appearing in an HF calculation will be all that are required. The energy eigenvalue equation reduces to a set of simultaneous linear equations in the parameters and they may be obtained in a single diagonalisation process. No recycling procedure is required in order to obtain self-consistency. Further, prior knowledge of excited states of the true or of a model Hamiltonian is not required, as in CI or MBPT methods.

In ultimate analysis the present approach will be equivalent to a full CI calculation with a given basis set.

It is pertinent to mention here a calculation on a similar framework done by Harris and Pohl (1965). Their interest was on properly reproducing the Morse potential for diatomic molecules at large internuclear distances. They used split-shell orbitals and obtained the single particle MO's from a correlated two-particle

wave function. This was possible since in their case the number of independent parameters in the two descriptions were equal. For internuclear separations close to equilibrium value they obtained complex MO coefficients. This implied relative phase differences between the AO's.

Another similar calculation illustrating the inter-particle correlation aspect was performed by Sengupta and Mukherji (1968). Starting from the HF framework and following a procedure similar to what has been described here it was possible to calculate the van der Waals force constant between inert gas atoms. Under strict HF approximation it should have been zero, since the origin of the van der Waals force between two non-overlapping atoms lie in the instantaneous correlation of the electrons in the two charge clouds.

2. Theory

We shall demonstrate our approach by a simple model. Consider a He atom in the singlet ground state, for which the HF eigenstate may be represented as

$$\psi_{HF}(1, 2) = \phi(1)\phi(2) \tag{4}$$

Here ϕ is the one-particle 1s orbital of He. The antisymmetric combination of the two spin functions has been omitted for simplicity. Let the orbital ϕ be built out of two normalized Slater-type basis functions χ_1 and χ_2 with real coefficients b. Thus

$$\phi = b_1\chi_1 + b_2\chi_2 \tag{5}$$

Then

$$\psi_{HF}(1, 2) = b_1{}^2\chi_1(1)\chi_1(2) +$$
$$+ b_1b_2\{\chi_1(1)\chi_2(2) + \chi_2(1)\chi_1(2)\} + b_2{}^2\chi_2(1)\chi_2(2) \tag{6}$$

For this system the correlated function following eq (3) will be

$$\psi_{corr}(1, 2) = c_1\chi_1(1)\chi_1(2) + c_2\chi_1(1)\chi_2(2) +$$
$$+ c_2'\chi_2(1)\chi_1(2) + c_3\chi_2(1)\chi_2(2) \tag{7}$$

It looks similar to the Weinbaum (1933) wavefunction of the form (VB + Ionic), if the χ's are the AO's. Pauli exclusion principle requires $c_2' = c_2$ for the singlet configuration. Comparing equations (6) and (7) we note that if the number of independent parameters in the two equations are same, then it is possible to obtain the b's from the c's and *vice versa*. Such a situation arises in a DODS (Löwdin 1964) or a split-shell representation (Harris and Pohl 1965) of molecular orbitals built out of two AO's only. In general the number of c parameters will exceed the number of b parameters and additional restraints on the former will be required in order to make the two functions equivalent. Between the above two functions (6) and (7) this relation is

$$c_1c_3 = c_2{}^2 \tag{8}$$

Relaxation of such relations constitutes the essential spirit of the present approach.

If we try to expand (7) in terms of functions of type (6), *i.e.*, products of s-type orbitals taken two at a time, it would look like a linear combination of such functions. If the s-type orbitals are chosen to be the He *ns* functions, the function (7) will be a radial-configuration-mixed representation for the ground state of He.

We propose to calculate the energy levels of the He atom with a set of ns-type basis orbitals. With only two bases the radially correlated wavefunction is

$$\psi_{\text{corr}}(1, 2) = c_1 g_1(1, 2) + c_2 g_2(1, 2) + c_3 g_3(1, 2) \tag{9}$$

where the normalised two-electron functions are

$$g_1(1, 2) = \chi_1(1)\,\chi_1(2)$$
$$g_2(1, 2) = (2 + 2S^2)^{-\frac{1}{2}}\{\chi_1(1)\,\chi_2(2) + \chi_2(1)\,\chi_1(2)\}$$
$$g_3(1, 2) = \chi_2(1)\,\chi_2(2)$$

with $\quad S = \langle \chi_1(1) \mid \chi_2(1) \rangle$ $\hspace{4cm}$ (10)

The normalisation constraint is

$$\sum_{ij} c_i c_j \mathscr{S}_{ij} = 1 \tag{11}$$

where $\mathscr{S}_{ij}$ is the ij-th element of the overlap matrix S, and the energy may be expressed as

$$E = \langle \psi_{\text{corr}}(1, 2) \mid \mathscr{H} \mid \psi_{\text{corr}}(1, 2) \rangle = \sum_{ij} c_i c_j \mathscr{H}_{ij}. \tag{12}$$

We obtain the energy values by solving the equation

$$\mathsf{H}c = \mathsf{S}cE \tag{13}$$

3. Results

3.1. Helium atom

The results of our calculation are given in table 1. The salient features are enumerated below.

Table 1. Energy of He atom in ground state (E_0) and in first two excited s-states (E_1 and E_2) including radial correlation. All energies are in a.u.

| Basis orbitals[a] | Number of 2-electron functions | E_{Hr} | Correlated energy values | | |
Serial No			E_0	E_1	E_2
1, 2	3	−2·8034	−2·8732	−0·1562	2·1407
1–3	6		−2·8776	−0·9577	0·6216
1–4	10		−2·8785	−2·0517	−0·7036
Clementi[b]	10	−2·86168	−2·8786	−2·1016	−0·7260
1–5	15		−2·8787	−2·1360	−1·7267
Clementi[c]	15	−2·86168	−2·87890	−2·0796	−0·8573
Weiss[d]		−2·86168	−2·87896		
1–6	21		−2·87899	−2·1441	−2·0243
Theoretical limit for radial correlation[e]			−2·87900		
Experimental[f]			−2·9038	−2·1461	−2·0614

[a] *vide* table 2; [b] 4 basis orbitals. Exponents optimised to represent HF 1s orbital. Taken from Clementi (1965), Table 03–01; [c] 5 basis orbitals. Clementi (1965), Table 01-01; [d] Weiss (1961), Table II; [e] Estimated by Shull and Löwdin (1959); [f] Moore (1949).

The calculation with two bases with exponents chosen arbitrarily (*i.e.*, reasonable guess, without an attempt to optimise them) yields poor HF ground state energy ($-2\cdot8034$ a.u.) as expected. But inclusion of radial correlation yields a value ($-2\cdot8732$ a.u.) even better than the HF energy ($-2\cdot8617$ a.u.) with 5 optimised exponents (Clementi 1965). We may infer that inclusion of correlation with an approximate basis set gives better representation of the system than a HF description with improved bases. However, it is not intended to imply that improvement of basis is unimportant. It only goes to show that from the physical point of view more attention should be given to the Hamiltonian itself. One should first try to include as much of the Hamiltonian as possible under a particular framework of calculation. Finer improvement on the basis set should come next. It has also been mentioned by other workers that choice of the basis set is not always very critical (*see* for example, Nesbet and Watson 1958).

Next, we observe that explicit inclusion of 2s-type orbitals do not significantly improve the ground state energy E_0. This is because the two-electron functions g allow independent freedom to the electron pair to exist simultaneously at different regions of space. Thus the correlated charge density with 1s-type bases can simulate to a large extent that corresponding to a HF $(2s)^2$ configuration. Hence, if our interest is confined only to the ground state we may safely work with a reasonably good set of 1s-type bases.

However, the behaviour of the higher energy states E_1 or E_2 is critically dependent upon the basis set used. Addition of 2s-type orbitals to the set improve these energy values remarkably. Further improvements, particularly on E_2, is expected when we add a few 3s-type orbitals. Hence, to study excited states with a finite basis set, one has to be careful to include such basis functions as will be able to span the higher order configuration space.

Finally, we note that the experimental ground state energy of He is $-2\cdot9038$ a.u. (Moore 1949). Taking E_{NR} to be roughly equal to it, we find that nearly half of the correlation energy is explained by the radial correlation alone as described here. The angular correlation is likely to account for a substantial portion of the remaining half.

We obtain for the radially correlated ground state energy the value of $-2\cdot87899$ a.u., which is about the limiting value of $-2\cdot87900$ a.u. set by Shull and Löwdin (1959). Weiss (1961) also obtained a similar value of $-2\cdot87896$ a.u. for the s-function contribution for He.

We would like to make a few comments on inclusion of angular correlation in the calculation of this type. Following the standard configuration mixing procedure we may add configurations involving orbitals with different angular dependence to the HF ground state. Then we may build radially correlated functions on each such mixed configuration. The totality will represent a fully correlated description of the system. Such a description will maintain all the advantages of the present approach including ultimate mathematical simplicity. A pilot calculation based on this line of approach is on way and results will be reported in due course.

3.2. H⁻ *ion*

The hydride ion is of particular interest. The second electron is very loosely bound to H atom. The HF theory fails to reproduce this bound state. Interelectronic correlation plays an essential role in keeping the electron bound to the host atom. The ground state energy of H⁻ ion has been calculated with 4 basis orbitals χ_{1s}, *i.e.*, with 10 two-electron product functions g. The value obtained is $E_0 = -0.5143$ a.u. Compared to $E_{HF} = -0.4881$ a.u. this gives the radial correlation correction to ground state energy $E_{corr} = -0.0262$ a.u. Weiss (1961) in his calculation for H⁻ with s-functions only obtained $E_0 = -0.51439$ a.u. in close agreement with ours. Further, the electron affinity of H as obtained by us is -0.0143 a.u., which is better than the value of -0.0138 a.u. obtained by Goddard (1968) and of -0.0133 a. u. calculated by Shull and Löwdin (1956). Inclusion of angular correlation is likely to further improve our value of electron affinity.

Table 2. Ground state radially correlated energy (E_0) for 2-electron ions, non-relativistic energy (E_{NR}) and percentage of total correlation energy (E_{corr}) explained by radial correlation alone

Ion	E_{HF}[a]	E_0 Present calculation[b]	Weiss[c]	E_{NR}[d]	Percentage explained[e]
Li⁺	− 7·2364	− 7·2521	−7·25242	− 7·27991	36
Be²⁺	−13·6113	−13·6262		−13·65557	34
B³⁺	−21·9862	−22·0008		−22·03097	33
C⁴⁺	−32·3612	−32·3767		−32·40625	34
N⁵⁺	−44·7361	−44·7499		−44·78145	30
O⁶⁺	−59·1111	−59·1259	−59·12595	−59·15660	33

[a] Taken from Clementi (1965), Table 03–01; [b] Orbital parameters taken from Clementi (1965), 4 basis orbitals, *i.e.*, 10 two-electron functions each; [c] Weiss (1961), Table 2; [d] Calculated by Pekeris (1958). Values quoted from Weiss (1961), Table 1; [e] Percentage = $100 \times (E_0 - E_{HF})/(E_{NR} - E_{HF})$.

Table 3. Orbital exponents for calculations reported in tables 1 and 2

Sl No	Type	Orbital exponents[a]							
		H⁻	He	Li⁺	Be²⁺	B³⁺	C⁴⁺	N⁵⁺	O⁶⁺
1	1s	1·3554	2·5	2·45161	3·42034	4·40720	5·39609	6·38688	7·37946
2	1s	1·0967	1·5	4·38942	4·82750	5·99281	7·23874	8·56040	9·95289
3	1s	0·4448	4·5	6·03853	8·32668	10·42220	12·47670	14·49340	16·47540
4	1s	0·2000	0·8	1·26508	1·83148	2·45924	3·09290	3·73216	4·37672
	2s		0·8						
6	2s		0·5						

[a] Values for Li⁺ to O⁶⁺ taken from Clementi (1965), Table 03–01.

Table 4. Values of coefficients (C_i) of eq. (9)

	H⁻	He	Li⁺	Be²⁺	B³⁺	C⁴⁺	N⁵⁺	O⁶⁺
1, 1	−0·82686	−0·12631 (+1)ᵃ	0·41964	−0·10617	−0·17113	−0·13450	−0·94649 (2)	0·10622
1, 2	0·22540 (+1)	0·40278 (+1)	0·11614 (+1)	0·19170 (+1)	0·20461 (+1)	0·19985 (+1)	0·17878 (+1)	0·15976 (+1)
1, 3	−0·35391	0·45852	−0·33930	−0·22076	−0·22547	−0·22698	−0·21454	−0·21122
1, 4	−0·84738 (−1)	−0·23726 (+1)	0·10356	0·20429	0·23741	0·24696	0·22664	0·21371
1, 5		0·1095 (+1)						
1, 6		−0·16058						
2, 2	−0·16716 (+1)	−0·32847 (+1)	−0·82816	−0·93205	−0·97820	−0·95416	−0·85830	−0·77611
2, 3	0·11920 (+1)	−0·51118	0·74031	0·34919	0·33003	0·31872	0·29914	0·29231
2, 4	0·49867	0·65853 (+1)	−0·68323 (−1)	−0·16005	−0·19329	−0·20613	−0·19086	−0·18270
2, 5		−0·29349 (+1)						
2, 6		0·41384						
3, 3	−0·65555 (−1)	−0·66711 (−1)	−0·19715	−0·55559 (−1)	−0·47738 (−1)	−0·44499 (−1)	−0·42368 (−1)	−0·42724 (−1)
3, 4	0·89605 (−1)	0·34017	0·25258 (−1)	0·23529 (−1)	0·25661 (−1)	0·27320 (−1)	0·26114 (−1)	0·27355 (−1)
3, 5		−0·16445						
3, 6		0·23979 (−1)						
4, 4	−0·21846 (−1)	−0·34945 (+1)	−0·26004 (−1)	−0·26009 (−1)	−0·28602 (−1)	−0·29732 (−1)	−0·27954 (−1)	−0·27820 (−1)
4, 5		0·34649 (+1)						
4, 6		−0·47956						
5, 5		−0·98978						
5, 6		0·29350						
6, 6		−0·25186 (−1)						

The first column gives the basic orbital pairs followed by serial numbers.

ᵃ$(\pm x) = 10^{\pm x}$.

The correlation energy of H^- has also been calculated by Dutta *et al* (1970) by the MBPT method. They obtain -0.0204 a.u. as the contribution from the $l = 0$ terms only. The numerical magnitude appears to be rather low since it does not yield the electron affinity in agreement with other calculations quoted above. However, for the total correlation energy their value is in agreement with those of other workers.

3.3. *2-electron positive ions*

The results of our calculation for 2-electron ions of Li to O in ^1S state are presented in table 2. In view of earlier discussion this calculation for the correlation in the ground state was performed with unaugmented 1s-type basis orbitals. The values of the parameters were taken from the HF ground state calculation of Clementi (1965). 4 basis functions with optimised exponents were used for each ion. Thus we obtained 10 two-electron functions for our calculation. A comparison of E_0 values in table 1 for the two Clementi functions with 4 and 5 parameters shows that discrepancy appears in the fourth place after decimals. Our results of table 2 are, therefore, correct upto the third place after decimal. They show a uniform tendency of accounting for one-third of the total correlation energy. The rest comes from angular correlation.

The values of the orbital exponents used in our calculation are listed in table 3. The combining coefficients c_i for the two electron functions g_i built out of various pairs of basis orbitals are given in table 4.

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