

# On the Orthogonality Problem for Excited States\*

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## 1. INTRODUCTION

SHARMA and Coulson<sup>1</sup> have shown that to first order in  $Z^{-1}$ ,  $Z$  being the nuclear charge, the Hartree-Fock wave functions of a pair of states of the same symmetry are orthogonal, and they have conjectured that the result is true to higher order. We shall show that, in fact, a departure from orthogonality occurs in second order.

## 2. DEPARTURE FROM ORTHOGONALITY

We consider as an example the  $1sns^2S$  states of the helium sequence. Denoting the  $1s, ns$  radial functions by  $u, v$  which may be assumed without loss of generality to be orthonormalized, we may write the complete (spatial) eigenfunction as

$$\psi_1(1sns) = (1/\sqrt{2})\{u(1)v(2) - u(2)v(1)\} \quad (1)$$

and the corresponding energy

$$E(1sns) = \langle u|H|u \rangle + \langle v|H|v \rangle + \langle uu|vv \rangle - \langle uw|uw \rangle, \quad (2)$$

where

$$\left. \begin{aligned} H &= -\frac{1}{2} \frac{d^2}{dr^2} - \frac{1}{r} \frac{d}{dr} - \frac{Z}{r}, \\ \langle ab| &= \frac{1}{r} \int_0^r a(t)b(t)t^2 dt + \int_r^\infty a(t)b(t)t dt, \\ \text{and} \\ \langle ab|cd \rangle &= \int_0^\infty \langle ab|c(r)d(r)r^2 dr. \end{aligned} \right\} \quad (3)$$

Now consider some other state, say  $1s'ms \dots^3S$ , whose orbitals are  $u', w$ . The complete eigenfunction for this state will be

$$\psi_2(1s'ms) = (1/\sqrt{2})\{u'(1)w(2) - u'(2)w(1)\} \quad (4)$$

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<sup>1</sup> C. S. Sharma and C. A. Coulson, Proc. Phys. Soc. (London), **80**, 81 (1962).

and its overlap with  $\psi_1$  is

$$S = \{\langle u|u'\rangle\langle v|w \rangle - \langle u|w\rangle\langle v|u'\rangle\}. \quad (5)$$

If  $u$  and  $v$  are varied in (2) without further restriction, we obtain the pair of Hartree-Fock equations

$$\left. \begin{aligned} Hu + \langle v|u \rangle - \langle uw|v \rangle &= \epsilon(1s)u \\ Hv + \langle uw|v \rangle - \langle uw|u \rangle &= \epsilon(ns)v \end{aligned} \right\} \quad (6)$$

and similarly for the state  $1s'ms^3S$ ,

$$\left. \begin{aligned} Hu' + \langle uw|u' \rangle - \langle u'w|w \rangle &= \epsilon'(1s)u' \\ Hw + \langle u'u'|w \rangle - \langle u'w|u' \rangle &= \epsilon(ms)w. \end{aligned} \right\} \quad (7)$$

We now expand

$$\left. \begin{aligned} u &= u_0 + Z^{-1}u_1 + \dots \\ \epsilon &= \epsilon_0 + Z^{-1}\epsilon_1 + \dots \\ \text{so that} \quad \langle ab| &= Z^{-1}\langle a_0b_0| + \dots \\ \text{and} \quad S &= S_0 + Z^{-1}S_1 + \dots \end{aligned} \right\} \quad (8)$$

and derive the following zero-order equations:

$$\left. \begin{aligned} (H - \epsilon_0(1s))u_0 &= 0 \\ (H - \epsilon_0(ns))v_0 &= 0 \end{aligned} \right\} \quad (9)$$

$$\left. \begin{aligned} (H - \epsilon'_0(1s))u'_0 &= 0 \\ (H - \epsilon'_0(ms))w'_0 &= 0 \end{aligned} \right\} \quad (10)$$

$$S_0 = \{\langle u_0|u'_0\rangle\langle v_0|w_0 \rangle - \langle u_0|w_0\rangle\langle v_0|u'_0 \rangle\}. \quad (11)$$

We see that  $u_0, v_0, w_0$ , are simply hydrogenic solutions for the states  $1s, ns, ms$  with corresponding hydrogenic eigenvalues, and it is clear that

$$u'_0 = u_0, \quad \epsilon'_0(1s) = \epsilon_0(1s), \quad (12)$$

so that we may drop the primes from these zero-order quantities. The functions  $u_0, v_0, w_0$ , automatically satisfy the orthonormality conditions

$$\left. \begin{aligned} \langle u_0|u_0 \rangle &= \langle v_0|v_0 \rangle = \langle w_0|w_0 \rangle = 1 \\ \langle u_0|v_0 \rangle &= \langle v_0|w_0 \rangle = \langle w_0|u_0 \rangle = 0 \end{aligned} \right\} \quad (13)$$

so that  $S_0 = 0$ .

The first-order equations may now be written

down:

$$\left. \begin{aligned} (H - \epsilon_0(1s))u_1 + \langle v_0 v_0 | u_0 - \langle u_0 v_0 | v_0 = \epsilon_1(1s)u_0, \\ (H - \epsilon_0(ns))v_1 + \langle u_0 u_0 | v_0 - \langle u_0 v_0 | u_0 = \epsilon_1(ns)v_0, \end{aligned} \right\} (14)$$

$$\left. \begin{aligned} (H - \epsilon_0(1s))u'_1 + \langle u_0 w_0 | u_0 - \langle u_0 w_0 | w_0 = \epsilon'_1(1s)u_0, \\ (H - \epsilon_0(ms))w_1 + \langle u_0 u_0 | w_0 - \langle u_0 v_0 | u_0 = \epsilon_1(ms)w_0, \end{aligned} \right\} (15)$$

and

$$\begin{aligned} S_1 &= \{ \langle u_0 | u_0 \rangle [ \langle v_0 | w_1 \rangle + \langle v_1 | w_0 \rangle ] \\ &\quad + [ \langle u_0 | u'_1 \rangle + \langle u_1 | u_0 \rangle ] \langle v_0 | w_0 \rangle \\ &\quad - \langle u_0 | w_0 \rangle [ \langle v_0 | u'_1 \rangle + \langle v_1 | u_0 \rangle ] \\ &\quad - [ \langle u_0 | w_1 \rangle + \langle u_1 | w_0 \rangle ] \langle v_0 | u_0 \rangle \} \\ &= [ \langle v_0 | w_1 \rangle + \langle v_1 | w_0 \rangle ] \end{aligned} \quad (16)$$

on account of (10).

The first-order solutions are arbitrary to within additive multiples of the corresponding zero-order solutions, and we choose those solutions which yield functions normalized up to first order. This is equivalent to the conditions

$$\langle u_0 | u_1 \rangle = \langle v_0 | v_1 \rangle = \langle u_0 | u'_1 \rangle = \langle w_0 | w_1 \rangle = 0. \quad (17)$$

Now from (14) and (15), using the Hermitean property of  $H$  as well as (9) and (10), we have

$$[\epsilon_0(ns) - \epsilon_0(ms)] \langle v_0 | w_1 \rangle = \langle u_0 v_0 | u_0 w_0 \rangle - \langle u_0 u_0 | v_0 w_0 \rangle$$

and

$$[\epsilon_0(ms) - \epsilon_0(ns)] \langle v_1 | w_0 \rangle = \langle u_0 v_0 | u_0 w_0 \rangle - \langle u_0 u_0 | v_0 w_0 \rangle \quad (18)$$

so that

$$[\epsilon_0(ms) - \epsilon_0(ns)] [ \langle v_0 | w_1 \rangle + \langle v_1 | w_0 \rangle ] = 0. \quad (19)$$

For  $m \neq n$ , this establishes that  $S_1 = 0$  for every pair of configurations  $1s \ ns \ ^3S$  and  $1s' \ ms \ ^3S$  in agreement with Sharma and Coulson.

It may be shown by straightforward analysis that orthogonality breaks down at second order; in fact,

$$\begin{aligned} S_2 &= \{ [ \langle v_0 | w_2 \rangle + \langle v_1 | w_1 \rangle + \langle v_2 | w_0 \rangle ] \\ &\quad - [ \langle u_0 | w_1 \rangle + \langle u_1 | w_0 \rangle ] [ \langle v_0 | u'_1 \rangle + \langle v_1 | u_0 \rangle ] \}, \end{aligned} \quad (20)$$

which may be written alternatively as

$$\begin{aligned} S_2 &= \{ [ \epsilon_0(ms) - \epsilon_0(1s) ] [ \epsilon_0(ns) - \epsilon_0(1s) ] [ \langle u_0 v_0 | w_0 \Delta u_1 \rangle \\ &\quad + \langle u_0 w_0 | v_0 \Delta u_1 \rangle - 2 \langle v_0 w_0 | u_0 \Delta u_1 \rangle ] \\ &\quad - [ \epsilon_0(ms) - \epsilon_0(ns) ] [ \langle u_0 w_0 | v_0 w_0 \rangle - \langle u_0 v_0 | w_0 w_0 \rangle ] \\ &\quad \times [ \langle u_0 v_0 | v_0 w_0 \rangle - \langle u_0 w_0 | v_0 v_0 \rangle ] \\ &\quad / \{ [ \epsilon_0(ms) - \epsilon_0(1s) ] [ \epsilon_0(ns) - \epsilon_0(1s) ] \\ &\quad \times [ \epsilon_0(ms) - \epsilon_0(ns) ] \} \end{aligned} \quad (21)$$

with

$$\Delta u_1 = u'_1 - u_1.$$

That a departure from orthogonality does occur is not unexpected for  $\psi_1$  and  $\psi_2$  are eigenfunctions of different Hamiltonians. Although the departure, being of second order, will usually be small<sup>2</sup> it may be serious in calculations of the probabilities of weak transitions.

It is obvious that wave functions obtained by solving the Schrödinger equation by perturbation methods will be automatically orthogonal to any given order, but an explicit demonstration may be instructive.

Suppose that the Hamiltonian  $H$  is decomposed according to

$$H = H_0 + H_1, \quad (22)$$

and that we have two eigenfunctions of  $H_0$  satisfying

$$H_0 u_0 = E_0 u_0 \quad (23)$$

and

$$H_0 v_0 = \epsilon_0 v_0, \quad (24)$$

such that

$$E_0 \neq \epsilon_0.$$

It follows that

$$S_0 \equiv \langle u_0 | v_0 \rangle = 0, \quad (25)$$

and we shall prove that

$$S_n \equiv \sum_{i=0}^n \langle u_i | v_{n-i} \rangle = 0 \quad (26)$$

for each  $n$  in turn.

We write the general perturbation equations in the form

$$H_0 u_n + H_1 u_{n-1} = \sum_{s=0}^n E_s u_{n-s} \quad (27)$$

and

$$H_0 v_n + H_1 v_{n-1} = \sum_{i=0}^n \epsilon_i v_{n-i}, \quad (28)$$

and adopt the convention that  $u_{-i} = v_{-i} = 0 (i > 0)$ .

From (27) with  $n = i$  and (28) with  $n = n - i$ , we have

$$\langle v_{n-i} | H_0 | u_i \rangle + \langle v_{n-i} | H_1 | u_{i-1} \rangle = \sum_{s=0}^n E_s \langle v_{n-i} | u_{i-s} \rangle \quad (29)$$

<sup>2</sup> Dr. C. Froese (private communication, 1963) finds that  $(\psi_1, \psi_2)$  is  $9 \times 10^{-4}$  for the sodium configurations  $1s^2 2s^2 2p^6 3s$  and  $1s^2 2s^2 2p^6 4s$  and  $5 \times 10^{-4}$  for  $1s^2 2s^2 2p^6 3p$  and  $1s^2 2s^2 2p^6 4p$ .

and

$$\langle u_i | H_0 | v_{n-i} \rangle + \langle u_i | H_1 | v_{n-i-1} \rangle = \sum_{i=0}^{n-i} \epsilon_i \langle u_i | v_{n-i-i} \rangle; \quad (30)$$

then subtracting (30) from (29), using the Hermitean properties of  $H_0$  and  $H_1$ , and summing over  $i$  from 0 to  $n$ , we have

$$0 = \sum_{i=0}^n \sum_{s=0}^i E_s \langle v_{n-i} | u_{i-s} \rangle - \sum_{i=0}^n \sum_{t=0}^{n-i} \epsilon_t \langle u_i | v_{n-i-t} \rangle. \quad (31)$$

These finite double sums may be rewritten so that (31) becomes

$$0 = \sum_{s=0}^n (E_s - \epsilon_s) \sum_{i=0}^{n-s} \langle u_i | v_{n-s-i} \rangle \quad (32)$$

and (26) follows by induction.

This result is valid only for the *exact* solutions  $u_n, v_n$  of the perturbation equations; if the Eqs. (27) and (28) are solved by the variation technique  $u_n$  and  $v_n$  are not exact solutions and the orthogonality condition (26) may not be satisfied. Condition (26) then provides an additional criterion of the accuracy of the procedure and the resulting  $n$ th-order corrections to the eigenfunctions  $u, v$ .

## Statistical Theory of Atoms

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### 1. THE STATISTICAL FIELD EQUATION (T. F. EQUATION)

BY 1925 some effective electric fields inside atoms had been calculated to fit observed data.<sup>1</sup> The Bohr-Sommerfeld theory<sup>2</sup> gave orbits in a spherically symmetrical field with definite energies for the series electron and for inner electrons. Pauli's equivalence principle<sup>3</sup> requiring that there are never two electrons in an atom with all their quantum numbers the same, coupled with the discovery of electron spin,<sup>4</sup> allowed just two electrons with opposite spins to occupy an orbit in the field. The field could then be adjusted to give, using Bohr's frequency condition, for outer normally unoccupied orbits, and for inner normally occupied orbits, respectively, approximations to the optical spectrum and to the x-ray spectrum.

The Bohr-Sommerfeld orbits correspond to successive discrete values of action variables, differing by Planck's constant  $h$ , which, with their conjugate phases, give a canonical mapping of the phase-space of the electron. Thus if each orbit is occupied by two electrons, these are distributed rather uniformly at two for each  $h^3$  of six-dimensional configuration-momentum space. We need now suppose only that the electrons present fill the orbits of lowest energy

in the effective field, so that if  $V$  is the potential in that field, measured from a suitable zero, electrons may have momentum up to  $(2 \text{ meV})^{\frac{1}{2}}$ , where  $m$  and  $e$  are electron mass and charge, and may occupy volume  $\frac{4}{3} \pi (2 \text{ meV})^{\frac{3}{2}}$  of momentum space, to obtain the value for the charge density at a place with potential  $V$ ,

$$\rho = -e \frac{2}{h^3} \frac{4}{3} \pi (2 \text{ meV})^{\frac{3}{2}}.$$

Assuming also Poisson's equation, we have

$$\nabla^2 V = -4\pi\rho = 4\pi e \frac{2}{h^3} \frac{4}{3} \pi (2 \text{ meV})^{\frac{3}{2}},$$

as an approximate equation for the potential of the effective electric field in an atom.<sup>5</sup> For a neutral atom we will expect  $V \rightarrow 0$  as  $r \rightarrow \infty$  and  $Vr \rightarrow Z$ , the nuclear charge, as  $r \rightarrow 0$ , as boundary conditions at infinite and zero radius  $r$ .

This field gives the structure of the periodic table, the total binding energies of atoms, their spectra, and atomic scattering cross sections—all in rough qualitative agreement with observation. Its advantage is its simplicity, one integration sufficing by scaling for all neutral atoms. Its disadvantage is its roughness.

In "atomic units,"  $h = 2\pi$ ,  $e = 1$ ,  $m = 1$ , we have the T.F. equation

$$\nabla^2 V = \frac{8\sqrt{2}}{3\pi} V^{\frac{3}{2}}. \quad (1)$$

<sup>1</sup> D. R. Hartree, Proc. Cambridge Phil. Soc. **21**, 615 (1924); E. Fues, Z. Physik **11**, 369 (1922).

<sup>2</sup> N. Bohr, Phil. Mag. **26**, 1 (1913); A. Sommerfeld, Ber. Akad. (München) 425 (1915).

<sup>3</sup> W. Pauli, Z. Physik **31**, 765 (1925).

<sup>4</sup> G. Uhlenbeck and S. Goudsmit, Naturwissenschaften, 957 (Nov. 1925).

<sup>5</sup> L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1927); E. Fermi, Z. Physik **48**, 73 (1928).