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While giving some lectures on the $1/Z$ Method we came upon a derivation of the form of the first order wave function which seems simpler than those now in the literature [For a summary see Sueng and Wilson, J. Chem. Phys. 47, 5343 (1967). Our method most closely resembles that of Sinanoğlu, Phys. Rev. 122, 491 (1961)]. Hence we wish to pass it on.

We will use $1s^2\,2s$ as an example but the generalization will be obvious. The first order wave function satisfies

$$(H^{(0)} - E^{(0)})\,\psi^{(1)} + (H^{(1)} - E^{(1)})\,\psi^{(0)} \qquad (1)$$

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where

$$H^{(0)} = \sum_{i=1}^{3} h(i)$$

$$h(i) = -\frac{1}{2}\nabla^2 - \frac{2}{r_i}$$

$$H^{(1)} = \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

$$E^{(1)} = (\psi^{(0)}, H^{(1)}\psi^{(0)})$$

$$\psi^{(0)} = \mathcal{A}\, s(1)s(2)\bar{s}(3)\,\alpha(1)\beta(2)\alpha(3)$$

$$\equiv \mathcal{A}\,\varphi^{(0)}\alpha(1)\beta(2)\alpha(3)$$

with $\mathcal{A}$ the antisymmetrizer, s and $\bar{s}$ respectively the 1s and 2s eigenfunctions of h, and $E^{(0)} = 2E(s) + E(\bar{s})$.

Now since $H^{(0)}$ and $H^{(1)}$ are symmetric and spin independent it is tempting to say, let us solve

$$(H^{(0)} - E^{(0)})\varphi^{(1)} + (H^{(1)} - E^{(1)})\varphi^{(0)} = 0 \qquad (2)$$

and then write

$$\psi^{(1)} = \mathcal{A}\,\varphi^{(1)}\alpha(1)\beta(2)\alpha(3) \qquad (3)$$

The difficulty of course is that (2), as it stands, is inconsistent since there are $\varphi^{(0)'}$ which are also eigenfunctions of $H^{(0)}$ with eigenvalue $E^{(0)}$, indeed $\varphi^{(0)}$ itself is an example, such that

$$(\varphi^{(0)'}, (H^{(1)} - E^{(1)})\varphi^{(0)}) \neq 0$$

To avoid these inconsistencies we replace (1) by

$$(H^{(0)} - \epsilon)\psi^{(1)} + (H^{(1)} - E^{(1)})\psi^{(0)} = 0 \qquad (4)$$

and take the limit $\epsilon \to E^{(0)}$ only at the end of the calculation. Now aside from making $(\psi^{(0)}, \psi^{(1)}) = 0$, which of course is quite permissible, AND INDEED IS THE USUAL CHOICE this procedure is quite innocuous. That is $\psi^{(1)}$ as defined by (4)) exhibits no singularities as $\epsilon \to E^{(0)}$, i.e. there are no terms proportional to $(E^{(0)} - \epsilon)^{-1}$ because there are no $\psi^{(0)'}$ which are eigenfunctions of $H^{(0)}$ with eigenvalue $E^{(0)}$ and such that

$$(\psi^{(0)'}, (H^{(0)} - E^{(1)})\psi^{(0)}) \neq 0$$

Now consider the analogue of (2), namely

$$(H^{(0)} - \epsilon)\varphi^{(1)} + (H^{(1)} - E^{(1)})\varphi^{(0)} = 0 \qquad (5)$$

As long as $\epsilon \neq E^{(0)}$ (or anyother eigenvalue) this is a perfectly consistent equation. However $\varphi^{(1)}$ evidently will contain $(E^{(0)} - \epsilon)^{-1}$ terms. Namely the $(\varphi^{(0)'}, \varphi^{(1)})$ will all depend on ϵ in this way. However since if we multiply (5) by $\alpha(1)\beta(2)\alpha(3)$, apply $\mathcal{A}$ and use (3), we recover (4), it follows that since $\psi^{(1)}$ contains no $(E^{(0)} - \epsilon)^{-1}$ terms, they must cancel identically on antisymmetrization, and hence we can ignore them in solving (5).

We now (for obvious reasons) write (5) as

$$(H^{(0)} - \epsilon)\,\varphi^{(1)} = \left(\frac{1}{r_{12}} - E^{(1)}(12) \right) \Lambda(1)\,\Lambda(2)\,\bar{\Delta}(3)$$

$$+ \frac{1}{\sqrt{2}} \left(\frac{1}{r_{13}} - E^{(1)}(13) \right) \frac{\Lambda(1)\,\bar{\Lambda}(3) - \bar{\Delta}(1)\,\Delta(3)}{\sqrt{2}}\,\Lambda(2)$$

$$+ \frac{1}{\sqrt{2}} \left(\frac{1}{r_{13}} - E^{(1)}(13) \right) \frac{\Lambda(1)\,\bar{\Delta}(3) + \bar{\Delta}(1)\,\Lambda(3)}{\sqrt{2}}\,\Lambda(2)$$

$$+ \frac{1}{\sqrt{2}} \left(\frac{1}{r_{23}} - E^{(1)}(23) \right) \frac{\Lambda(2)\,\bar{\Lambda}(3) - \bar{\Delta}(2)\,\Lambda(3)}{\sqrt{2}}\,\Lambda(1)$$

$$+ \frac{1}{\sqrt{2}} \left(\frac{1}{r_{23}} - E^{(1)}(23) \right) \frac{\Lambda(2)\,\bar{\Delta}(3) + \bar{\Delta}(2)\,\Lambda(3)}{\sqrt{2}}\,\Lambda(1)$$

+ NUMERICAL MULTIPLES OF $\Lambda(1)\,\Lambda(2)\,\bar{\Delta}(3)$, $\Lambda(1)\,\bar{\Lambda}(2)\,\Lambda(3)$ and $\bar{\Delta}(1)\,\Lambda(2)\,\Lambda(3)$

Here $E^{(1)}(1S)$ is the first order energy of the $1s^2$ state, thus

$$E^{(1)}(1S) = (AA, \tfrac{1}{r} AA)$$

etc.

One now readily sees that the only source of $(E^{(0)}-\epsilon)^{-1}$ terms is precisely the "numerical multiples" [There are no such that $\varphi^{(0)'}$ such that $(\varphi^{(0)'}, (\tfrac{1}{r_{12}} - E^{(1)}(1S))A(1)\alpha(1)A(2)\beta(2)\bar{A}(3)) \neq 0$ and similarly for the next four pieces], and further one sees that this is their only contribution [The solution of $(H^{(0)}-\epsilon)\chi + A\,A(1)A(2)\bar{A}(3)$ where A is a number is clearly just $\chi_2 - (E^{(0)}-\epsilon)^{-1} A\,A(1)A(2)\bar{A}(3)$] Thus, in accord with our previous discussion we may drop them and immediately find the known result that effectively

$$\varphi^{(1)} = \varphi^{(1)}_{12}(1S)\bar{A}(3) + \frac{1}{r_{12}}\left[\varphi^{(1)}_{13}(^3\bar{S}) + \varphi^{(1)}_{13}(^1\bar{S})\right]A(2) + \frac{1}{r_{12}}\left[\varphi^{(1)}_{23}(^3\bar{S}) + \varphi^{(1)}_{23}(^1\bar{S})\right]A(3)$$

Here, of course $\varphi^{(1)}_{12}(1S)$ is the first order correction to $1s^2\ {}^1S$ for electrons 1 and 2 etc.* [One may also check explicitly, if one wishes, that the "numerical multiple" terms are completely symmetric in 1, 2, 3 so that if one multiplies by $\alpha(1)\beta(2)\alpha(3)$ and applies $\hat{A}$ their contribution will vanish identically. However the point is that there is no need to do this. Our general argument proves that the cancelation must occur.]

* with $(A(1)A(2), \varphi^{(1)}_{12}(1S)) = 0$

We close with comments on a slightly different point. $\psi^{(0)}$ can be written

$$\psi^{(0)} = \frac{1}{\sqrt{3}} \Big[\frac{1}{\sqrt{2}} \big(\Delta(1)\Delta(2)\bar{\Delta}(3) - \bar{\Delta}(1)\Delta(2)\Delta(3) \big) \alpha(1)\beta(2)\alpha(3)$$

$$+ \frac{1}{\sqrt{2}} \big) \alpha(1)\alpha(2)\beta(3)$$

$$- \frac{1}{\sqrt{2}} \big) \beta(1)\alpha(2)\alpha(3) \Big]$$

Now in dealing with symmetric spin independent operators, for example $H^{(0)}$ and $H^{(1)}$, each of the spin parts in $\psi^{(0)}$ yields the same contribution and there are no cross terms. Hence we can replace $\psi^{(0)}$ by

$$\phi^{(0)} = \frac{1}{\sqrt{2}} \big(\Delta(1)\bar{\Delta}(3) - \bar{\Delta}(1)\Delta(3) \big) \Delta(2)$$

and the whole discussion goes through as before except that $\mathcal{A}$ is replaced by

$$\mathcal{A} = \frac{1 - P_{13}}{\sqrt{2}}$$

where P_{13} permutes the spatial coordinates of 1 and 3. In particular then

$$\phi^{(1)} = \mathcal{A}\, \psi^{(1)}$$

Further in calculating a matrix element of a spin independent symmetric operator we need apply $\mathcal{A}$ only once since $\mathcal{A}$ will commute with the operator, is Hermitian, and satisfies $\mathcal{A}^2 = \sqrt{2}\,\mathcal{A}$. Thus

for example

$$E^{(2)}_2 \quad (\psi^{(0)}, (H^{(1)} - E^{(1)})\, \psi^{(1)}) = (\phi^{(0)}, (H^{(1)} - E^{(1)})\, \phi^{(1)})$$

$$= \sqrt{2}\, (\phi^{(0)}, (H^{(1)} - E^{(1)})\, \varphi^{(1)})$$

which can considerably simplify the calculations.