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NOTE ON THE SYMMETRY OF PERTURBED HARTREE-FOCK AND

X-α WAVEFUNCTIONS

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ABSTRACT

It is shown that the first order orbitals for X-α or Hartree-Fock atoms perturbed by multipole electric fields have the expected symmetry properties.

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Recently it has been suggested[1] that the first order orbitals describing the perturbation of Hartree-Fock or X-α closed-shell atoms (more generally atoms with all occupied spatial shells closed) by a multipole electric field do not have the expected symmetry properties. In this note we will show that these fears are groundless. More precisely we will show that the assumption of the expected symmetry is a self-consistent one. This of course does not immediately show that it is the only solution of the perturbation equations, but since the latter are inhomogeneous <u>linear</u> equations, we expect that this is probably the case. [Ahlberg and Goscinski (private communication) have now also reached the same conclusion as regards X-α]

We consider the perturbation of an orbital $U^{(0)}_{n_i \ell_i m_i}$ of the form

$$U^{(0)}_{n_i \ell_i m_i}(\vec{1}) = Y_{\ell_i m_i}(\hat{1})\, R_{n_i \ell_i}(r_1) \tag{1}$$

by a perturbation proportional to $P_L(\hat{1})$ where $\vec{1}$ represents all the cartesian coordinates of particle 1 and where $\hat{1}$ is a unit vector in the $\vec{1}$ direction and hence represents the angular coordinates. Then writing

$$P_L(\hat{1}) Y_{\ell_i m_i}(\hat{1}) = \sum_j \sum_{m_j=-j}^{j} Y_{j m_j}(\hat{1}) (Y_{j m_j} , P_L Y_{\ell_i m_i}) \tag{2}$$

one expects[2] that the first order perturbed orbital will have the form

$$U^{(1)}_{n_i \ell_i m_i} = \sum_j R^{(1)}_{j n_i \ell_i L}(r_1) \sum_{m_j=-j}^{j} Y_{jm_j}(\hat{1})(Y_{jm_j}\ , P_L Y_{\ell_i m_i}) \tag{3}$$

To see whether or not this assumption is self-consistent we first examine the first-order correction to the charge density. The contribution from a closed-shell of orbital angular momentum k is then

$$\sum_{m_k=-k}^{k} U^{(1)}_{n_k k m_k}(\vec{1})\ U^{(0)*}_{n_k k m_k}(\vec{1}) + \text{c.c.} \tag{4}$$

and in turn the contribution to this from a given j in (3) is then, in its angular dependence, proportional to

$$Q^{L0}_{jk} + Q^{L0*}_{jk}$$

where

$$Q^{LM}_{jk}(\hat{1}) \equiv \sum_{m_k=-k}^{k} \sum_{m_j=-j}^{j} Y_{jm_j}(\hat{1})(Y_{jm_j}\ , Y_{LM} Y_{km_k}) Y^{*}_{km_k}(\hat{1}) \tag{5}$$

We will now prove that $Q^{LM}_{jk}(\hat{1})$ is an M independent multiple of $Y_{LM}(\hat{1})$ and this, as one can then readily verify, is sufficient to completely guarantee the consistency of our assumption as far as X-α is concerned, and, is sufficient for Hartree-Fock exclusive of the exchange terms. (Note for example that the potential produced by Q^{L0}_{jk} will also be proportional to $P_L(\hat{1})$) .

We first use the spherical harmonic addition theorem to rewrite (5), to within a constant factor as

$$Q_{jk}^{LM}(\hat{1}) = \int d\hat{2}\; P_j(\hat{1}\cdot\hat{2})Y_{LM}(\hat{2})P_k(\hat{1}\cdot\hat{2}) \tag{6}$$

It is then easy to show[3] that $Q_{jk}^{LM}(\hat{1})$ transforms under rotation precisely like $Y_{LM}(\hat{1})$ and hence as claimed must be an M-independent numerical multiple of $Y_{LM}(\hat{1})$. The numerical coefficient is evaluated in the appendix of this article.

Turning now to the exchange terms of Hartree-Fock, the contribution from a given j and k in the equation for $U^{(1)}_{n_i \ell_i m_i}$ is readily found to be the sum of two pieces one of which, insofar as is its angular dependence is concerned, being proportional to

$$T_{jk}^{L0}(\vec{1}) \tag{7}$$

and the other to

$$T_{kj}^{L0}(\vec{1})$$

where

$$T_{jk}^{LM}(\vec{1}) = \sum_{m_k=-k}^{k} \sum_{m_j=-j}^{j} \int \frac{d\hat{2}}{r_{12}} Y_{jm_j}(\hat{1})(Y_{jm_j}, Y_{LM}Y_{km_k})Y_{\ell_i m_i}(\hat{2})Y^*_{km_k}(\hat{2}) \tag{8}$$

We will now show that $T^{LM}_{jk}(\vec{1})$ is of the form

$$T^{LM}_{jk}(\vec{1}) = \sum_{\lambda} \rho^{jkL}_{\lambda \ell_i}(r_1) \sum_{\mu=-\lambda}^{\lambda} Y_{\lambda\mu}(\hat{1})(Y_{\lambda\mu}, Y_{LM}Y_{\ell_i m_i}) \tag{9}$$

where, as indicated, ρ is independent of μ,M and m_i. It is then easy to show that this is sufficient to ensure the consistency of the exchange term since with this result the m_i,μ dependent coefficients $(Y_{\lambda\mu}, P_L Y_{\ell_i m_i})$ will correctly cancel out of the equations one gets by equating the coefficient of each spherical harmonic separately equal to zero, the result in each case then being the same set of coupled equations for the radial functions $R^{(1)}_{jn_i\ell_i L}$.

To derive (9) we note that from the spherical harmonic addition theorem we have, to within an m_i,M independent factor that

$$T^{LM}_{jk}(\vec{1}) = \int \frac{d\hat{2}}{r_{12}} d\hat{3}\ P_j(\hat{1}\cdot\hat{3})P_k(\hat{2}\cdot\hat{3})Y_{LM}(\hat{3})Y_{\ell_i m_i}(\hat{2})$$

in which form it is clear[4] that under a rotation $T^{LM}_{jk}(\vec{1})$ transforms like $Y_{LM}(\hat{1})Y_{\ell_i m_i}(\hat{1})$. Hence writing $T^{LM}_{jk}(\vec{1})$ as

$$T^{LM}_{jk}(\vec{1}) = \sum_{\lambda}\sum_{\mu} Y_{\lambda\mu}(\hat{1})\ (Y_{\lambda\mu}, T^{LM}_{jk})$$

this means that (the argument is essentially the same as that in footnote 3)

$$\sum_{\mu} Y_{\lambda\mu}(\hat{1})(Y_{\lambda\mu}, T_{jk}^{LM}) = \frac{2\lambda+1}{4\pi}\int d\hat{2}\; P_{\lambda}(\hat{1}\cdot\hat{2})T_{jk}^{LM}(\hat{2})$$

transforms like $\sum_{\mu} Y_{\lambda\mu}(\hat{1})(Y_{\lambda\mu}, Y_{LM}Y_{\ell_i m_i})$ which in turn means, since the $Y_{\lambda\mu}$ for a given λ yield an irreducible representation of the rotation group, that to within a μ, M and m_i independent factor

$$(Y_{\lambda\mu}, T_{jk}^{LM}) = (Y_{\lambda\mu}, Y_{LM}Y_{\ell_i m_i}) \tag{10}$$

which proves the point. The coefficients $\rho_{\lambda\ell_i}^{jkL}$ are given explicitly in the appendix.

Our interest in these questions was aroused by conversations with R. Ahlberg. Also it is a pleasure to acknowledge further correspondence with him and Dr. Goscinski.

FOOTNOTES AND REFERENCES

1. R. Ahlberg and O. Goscinski, J. Phys. B. Atom. Molec. Phys. 6, 2254 (1973).

2. See for example A. Dalgarno, Adv. in Phys. 11, 281 (1962) Eq. (98).

3. Let $R\hat{1}$ denote the effect of rotating $\hat{1}$. Then evidently

$$Q_{jk}^{LM}(R\hat{1}) = \int d\hat{2}\ P_j(R\hat{1}\cdot\hat{2})Y_{LM}(\hat{2})\ P_k(R\hat{1}\cdot\hat{2})$$

$$= \int d\hat{2}\ P_j(\hat{1}\cdot R^{-1}\hat{2})Y_{LM}(\hat{2})\ P_k(\hat{1}\cdot R^{-1}\hat{2})$$

which upon changing variables according to $R^{-1}\hat{2}\to\hat{2}$ becomes

$$Q_{jk}^{LM}(R\hat{1}) = \int d\hat{2}\ P_j(\hat{1}\cdot\hat{2})Y_{LM}(R\hat{2})\ P_k(\hat{1}\cdot\hat{2})$$

which proves the point since the transformation coefficients are independent of coordinates.

4. Proceeding similarly as in 3 one finds that

$$T_{jk}^{LM}(R\vec{1}) = \int \frac{d\hat{2}}{r_{12}}\ d\hat{3}\ P_j(\hat{1}\cdot\hat{3})\ P_k(\hat{2}\cdot\hat{3})\ Y_{LM}(R\hat{3})\ Y_{\ell_i m_i}(R\hat{2})$$

which proves the point since the transformation coefficients are independent of coordinates.

5. A. Messiah, Quantum Mechanics, Vol. II (John Wiley & Sons, Inc., New York, 1966), Appendix C.

APPENDIX

We use the conventions of Messiah[5] in evaluating $Q_{jk}^{LM}(\hat{1})$ and $\rho_{\lambda\ell_i}^{jkL}(r_1)$ and refer to his equations. We evaluate $Q_{jk}^{LM}(\hat{1})$ of (6) by the spherical harmonic composition relation. From Messiah C.16 and C.17b one obtains

$$Q_{jk}^{LM}(\hat{1}) = 4\pi\begin{pmatrix} j & k & L \\ 0 & 0 & 0 \end{pmatrix}\sum_{\ell'}[(2L+1)(2\ell'+1)]^{1/2}\begin{pmatrix} j & k & \ell' \\ 0 & 0 & 0 \end{pmatrix}Y_{\ell'M}\sum_{m_j}\sum_{m_k}\begin{pmatrix} j & k & \ell' \\ m_j & m_k & -M \end{pmatrix}\begin{pmatrix} j & k & L \\ m_j & m_k & -M \end{pmatrix} .$$

The identity C.15a gives the desired result

$$Q_{jk}^{LM}(\hat{1}) = 4\pi\begin{pmatrix} j & k & L \\ 0 & 0 & 0 \end{pmatrix}^2 Y_{LM}(\hat{1}) \tag{A-1}$$

To evaluate $\rho_{\lambda\ell_i}^{jkL}(r_1)$ we note by comparing (9) and (10) it follows that

$$\rho_{\lambda\ell_i}^{jkL}(r_1)\ (Y_{\lambda\mu}, Y_{LM}Y_{\ell_i m_i}) = (Y_{\lambda\mu}, T_{jk}^{LM}) \tag{A-2}$$

We now evaluate the right hand side of this equation. From the definition (8) and Messiah C.16 it follows that

$$(Y_{\lambda\mu}, T_{jk}^{LM}) = (-)^{\mu}(4\pi)^{-1/2}(2_j+1)(2k+1)[(2\lambda+1)(2\ell_i+1)(2L+1)]^{1/2}\begin{pmatrix} j & k & L \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \sum_{\ell'} R_{\ell'}(r_1)\begin{pmatrix} \lambda & \ell' & j \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} k & \ell' & \ell_i \\ 0 & 0 & 0 \end{pmatrix}\sum_{m_j}\sum_{m_k}\sum_{m'}(-)^{m_j+m_k+m'}\begin{pmatrix} \lambda & \ell' & j \\ -\mu & -m' & m_j \end{pmatrix}\begin{pmatrix} k & \ell' & \ell_i \\ -m_k & m' & m_i \end{pmatrix}\begin{pmatrix} j & L & k \\ -m_j & M & m_k \end{pmatrix}$$

where

$$R_{\ell'}(r_1) = \int \frac{r_<^{\ell'}}{r_>^{\ell'+1}} \, r_2^2 \, dr_2$$

Use of Messiah C.33 then yields

$$(Y_{\lambda\mu}, T_{jk}^{LM}) = (-)^{\mu+L}(4\pi)^{-1/2}(2j+1)(2k+1)[(2\lambda+1)(2\ell_i+1)(2L+1)]^{1/2}$$

$$\times \begin{pmatrix} j & k & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_i & L & \lambda \\ m_i & M & -\mu \end{pmatrix} \sum_{\ell'} (-)^{\ell'} R_{\ell'}(r_1) \begin{pmatrix} \lambda & \ell' & j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k & \ell' & \ell_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell_i & L & \lambda \\ j & \ell' & k \end{Bmatrix} \qquad \text{(A-3)}$$

However

$$(Y_{\lambda\mu}, Y_{LM} Y_{\ell_i m_i}) = (-)^{\mu}(4\pi)^{-1/2}[(2\lambda+1)(2\ell_i+1)(2L+1)]^{1/2} \begin{pmatrix} \lambda & \ell_i & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_i & L & \lambda \\ m_i & M & -\mu \end{pmatrix}$$

$$\text{(A-4)}$$

and therefore, from (A-2), we have as our final result

$$\rho_{\lambda\ell_i}^{jkL}(r_1) = (-)^{L}(2j+1)(2k+1) \begin{pmatrix} \lambda & \ell_i & L \\ 0 & 0 & 0 \end{pmatrix}^{-1} \begin{pmatrix} j & k & L \\ 0 & 0 & 0 \end{pmatrix} \sum_{\ell'} (-)^{\ell'} R_{\ell'}(r_1) \begin{pmatrix} \lambda & \ell' & j \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} k & \ell' & \ell_i \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \ell_i & L & \lambda \\ j & \ell' & k \end{Bmatrix} \qquad \text{(A-5)}$$