N71-15938
NASA CR-116125

THEORETICAL CHEMISTRY INSTITUTE

THE UNIVERSITY OF WISCONSIN

ON THE SPHERICAL SYMMETRY OF THE EXCHANGE

POTENTIAL PRODUCED BY A CLOSED SHELL

Get DRF

by

Saul T. Epstein

WIS-TCI-327 13 November 1968

MADISON, WISCONSIN

ON THE SPHERICAL SYMMETRY OF THE EXCHANGE

POTENTIAL PRODUCED BY A CLOSED SHELL*

by

Saul T. Epstein

Theoretical Chemistry Institute and Physics Department,
University of Wisconsin, Madison, Wisconsin

- - - - -

* This research was supported by National Aeronautics and Space Administration Grant NGL 50-002-001.

While giving some lectures on the theory of Atomic Spectra, we came upon a simple direct proof of the spherical symmetry of the exchange potential produced by a closed shell. Since the standard texts (for example Condon and Shortley or Slater) give quite a different (and to us, far less transparent) proof, it seemed of interest to pass our proof along.

Using the spherical harmonic addition theorem, one readily finds that the exchange potential produced by a closed shell can be written as

$$V(\vec{R}_1, \vec{R}_2) = f(R_1, R_2)\, P_\ell(\cos\theta_{12})$$

where θ_{12} is the angle between $\vec{R}_1$ and $\vec{R}_2$.

$V(\vec{R}_1, \vec{R}_2)$ then appears in subsequent calculations as a non-local one-electron potential. That is if $\psi(\vec{R})$ and $\psi'(\vec{R})$ are one-electron functions, then one is interested in calculating quantities of the form

$$(\psi, V\psi') \equiv \int \psi^*(\vec{R}_1)\, V(\vec{R}_1, \vec{R}_2)\, \psi'(\vec{R}_2)\, d\vec{R}_1\, d\vec{R}_2$$

We will now show that V is spherically symmetric by showing that it commutes with the one-electron angular momentum $\vec{L} = \vec{R} \times \vec{p}$.

To this end we calculate

$$[L, V]\psi = \vec{L}_1 \int V(\vec{R}_1, \vec{R}_2)\, \psi(\vec{R}_2)\, d\vec{R}_2 - \int V(\vec{R}_1, \vec{R}_2)\, \vec{L}_2\, \psi(\vec{R}_2)\, d\vec{R}_2$$

which by an integration by parts, can be written as

$$[\vec{L}, V]\psi = \int [(\vec{L}_1+\vec{L}_2)V(\vec{R}_1,\vec{R}_2)]\psi(\vec{R}_2)d\vec{R}_2$$

We now observe that thought of as a two-electron wave function, $V(\vec{R}_1,\vec{R}_2)$, since it involves only the relative orientation of $\vec{R}_1$ and $\vec{R}_2$, is an S-state. Therefore

$$(\vec{L}_1+\vec{L}_2)V(\vec{R}_1,\vec{R}_2) = 0$$

whence we have

$$[\vec{L}, V]\psi = 0$$

for any ψ, which proves the point.