DECAY PROPERTIES OF SPATIAL MOLECULAR ORBITALS

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Abstract. Using properties of the Fourier transform we prove that if a Hartree-Fock molecular spatial orbital is in $L_1(\mathbb{R}^3)$, then it decays to zero as its argument diverges to infinity. The proof is rigorous, elementary, and short.

1. Introduction

We will use standard mathematical notation. In particular, $\mathbb{Z}$ will denote the set of integers and $\mathbb{R}$ the set of real numbers; if $r = (x_1, x_2, x_3) \in \mathbb{R}^3$, then $|r| = (x_1^2 + x_2^2 + x_3^2)^{\frac{1}{2}}$; If z is a complex number, z^* will denote its complex conjugate, and $\int f$ will stand for $\int_{\mathbb{R}^3} f$. For $1 \leq p < \infty$ we say that f is in $L_p(\mathbb{R}^3)$ (which we will abbreviate as L_p), if

$$\int_{\mathbb{R}^3} |f(r)|^p \, dr < \infty,$$

and the $L_p(\mathbb{R}^3)$ norm of f is defined by

$$||f|||_p = \left(\int_{\mathbb{R}^3} |f(r)|^p \, dr \right)^{1/p}.$$

We say that f is in $L_\infty(\mathbb{R}^3)$ (which we will abbreviate as L_∞) if there is a constant C such that $|f(r)| \leq C$ for all $r \in \mathbb{R}^3$. If f is in L_∞, the L_∞ norm is defined as

$$||f||_\infty = \sup |f(r)|, \qquad r \in \mathbb{R}^3,$$

(where"sup"is the least upper bound). We also define $h(r) = |r|^{-1}$; $\mathfrak{F}[f]$ or $\widehat{f}$ will stand for the Fourier transform of f; thus, if for instance $f \in L_1$, then

$$\widehat{f}(r) = \int_{\mathbb{R}^3} f(t) e^{-2\pi i r \cdot t} \, dt.$$

The convolution $f * g$ of f and g is defined by

$$(f * g)(r) = \int f(s) g(r - s) \, ds = \int f(r - s) g(s) \, ds,$$

and ∇^2 will denote the Laplace operator.

The functions $\psi_a, a = 1, \ldots, n$, where $n = N/2$ and N is the number of occupied spin orbitals, are spatial molecular orbitals; therefore they are continuous on $\mathbb{R}^3$

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and $||\psi_a||_\infty \le 1$, the sequence $\{\psi_a; a = 1, \ldots, n\}$ is orthonormal in L_2, and if Z_j is the atomic number of nucleus N_j, which is located at point $\xi_j \in \mathbb{R}^3$,

$$\begin{aligned}(1)\quad &\left[-\nabla^2 - \sum_{j=1}^{n} \frac{Z_j}{|r-\xi_j|}\right]\psi_a(r) + 2\sum_{c=1}^{n}\int |\psi_c(s)|^2 \frac{1}{|r-s|}\,ds\,\psi_a(r)\\ &\qquad - \sum_{c=1}^{n}\int \psi_c^*(s)\psi_a(s)\frac{1}{|r-s|}\,ds\,\psi_c(r) = \varepsilon_a\psi_a(r), \qquad a = 1, \ldots, n\end{aligned}$$

([2, 4]). The following auxiliary proposition, of some independent interest, shows that (1) is well posed:

Lemma 1. *If $f \in L_1 \cap L_\infty$, then*

$$||f * h||_\infty \le (4/\sqrt{3})\pi||f||_\infty + ||f||_1;$$

therefore, if $f, g \in L_2 \cap L_\infty$

$$||(fg) * h||_\infty \le (4/\sqrt{3})\pi||f||_\infty||g||_\infty + ||f||_2||\,||g||_2.$$

In particular,

$$\left|\int \psi_a^*(s)\psi_b(s)\frac{1}{|s-r|}\,ds\right| \le (4/\sqrt{3})\pi + 1, \qquad a, b = 1, \ldots, n.$$

Proof. We have

$$|(f*h)(r)| \le \int_{|s|\le 1} |f(r-s)|\,|s|^{-1}\,ds + \int_{|s|>1} |f(r-s)|\,|s|^{-1}\,ds = I_1 + I_2.$$

Applying Hölder's inequality and switching to spherical coordinates we get

$$I_1 \le \left(\int_{|s|\le 1} |f(r-s)|^2\,ds \int_{|s|\le 1} |s|^{-2}\,ds\right)^{\frac{1}{2}} \le (4/\sqrt{3})\pi||f||_\infty.$$

On the other hand,

$$I_2 \le ||f||_1.$$

□

The proof of the following theorem relies on basic properties of the Fourier transform ([1, 3]).

Theorem 1. *Let $\psi_a \in L_1$; then* $\lim_{r\to\infty}\psi_a(r) = 0$.

Proof. Equation (1) may be written in the equivalent form

$$[\nabla^2\psi_a](r) = g_a(r), \tag{2}$$

where

$$g_a(r) = -\sum_{j=1}^{n}\frac{Z_j}{|r-\xi_j|}\psi_a(r) + A\psi_a(r) - 2\sum_{c=1}^{n} B_{a,c}\psi_c(r) - \varepsilon_a\psi_a(r)$$

with

$$A = 2\sum_{c=1}^{n}\int |\psi_c(s)|^2\frac{1}{|r-s|}\,ds$$

and

$$B_{a,c} = \int \psi_c^*(s)\psi_a(s)\frac{1}{|r-s|}\,ds.$$

On the other hand, let K be arbitrary but fixed and such that $|\xi_j| \le K, j = 1, \ldots, n$; then

$$\int |r-\xi_j|^{-2}|\psi_a(r)|^2\,dr =$$
$$\int_{|r|\le K+1} |r-\xi_j|^{-2}|\psi_a(r)|^2\,dr + \int_{|r|>K+1} |r-\xi_j|^{-2}|\psi_a(r)|^2\,dr = J_1 + J_2.$$

We have:

$$J_1 \le \int_{|r|\le K+1} |r-\xi_j|^{-2}\,dr \le \int_{|r|\le K+1+|\xi_j|} |r|^{-2}\,dr = 4\pi(K+1+|\xi_j|)$$

and, since $|r| > K+1$ implies that $|r-\xi_j| \ge 1$,

$$J_2 \le \int_{|r|>K+1} |\psi_a(r)|^2\,dr \le ||\psi_a||_2^2,$$

which implies that $|r-\xi_j|^{-1}\psi_a(r)$ is in L_2 for all $1 \le j \le n$, which in turn implies that $g(r) \in L_2$. But $\psi_a \in L_1$ by hypothesis; thus

$$[\nabla^2\psi_a](r) = -4\pi^2|r|^2\widehat{\psi}_a(r).$$

Since ψ_a is bounded, it is in L_2 as well (and therefore so is $\widehat{\psi}_a$); thus (2) implies that $(1+|r|^2)\widehat{\psi}_a \in L_2$. Since

$$\widehat{\psi}_a(r) = \frac{1}{1+|r|^2}(1+|r|^2)\widehat{\psi}_a(r)$$

and $\frac{1}{1+|r|^2} \in L_2$, we deduce that $\widehat{\psi}_a \in L_1$, whence

$$\lim_{r\to\infty} \mathfrak{F}[\widehat{\psi}_a](r) = 0.$$

Since ψ_a is continuous on $\mathbb{R}^3$ we know that $\psi_a(r) = \mathfrak{F}[\widehat{\psi}_a](-r)$, and the assertion follows. □

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