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Incompleteness of atomic and molecular eigenfunctions

M.G. Marmorino

Department of Chemistry, Faculty of Science, Ubon Ratchathani University, Warinchamrap,
Ubon Ratchathani 34190, Thailand

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It is well known that the set of bound state hydrogenic eigenfunctions is not complete. Here we show that the set of bound state eigenfunctions for all atomic and molecular systems is incomplete in the Born–Oppenheimer approximation. A trivial argument that there are no positive eigenvalues is also presented which results from the virial theorem.

Shull and Löwdin argued that poor results for ground state energy calculations on helium using bound hydrogenic eigenfunctions are due to the incompleteness of the basis set [6]. Indeed, exact results can be approached using other basis sets. Here we show that the bound eigenfunctions for any atomic or molecular system in the Born–Oppenheimer approximation form an incomplete set.

We use the following three facts for an atomic or molecular Hamiltonian H.

1. Given $\varepsilon > 0$, for any spectral point λ of H, there exists a function $x \in \mathrm{Dom}(H)$ such that
$$\|(H-\lambda)x\| < \varepsilon. \tag{1}$$
This follows from the fact that H is a self-adjoint operator [2, theorem 5.10]. That H is self-adjoint was first proved by Kato [4].

2. Given a sequence $\{x_n\} \subset \mathrm{Dom}(H) \subset \mathbb{H}$, where $\mathbb{H}$ is Hilbert space, that converges to an $x \in \mathrm{Dom}(H)$, if there exists the sequence $\{Hx_n\} \subset \mathbb{H}$ that converges to a $y \in \mathbb{H}$, then $Hx = y$. This property is true for all closed linear operators [3]. Self-adjoint operators are closed [2, p. 50].

3. The electronic spectrum of H contains the interval $[0, \infty)$. Furthermore, this interval contains no eigenvalues. This was first proved by Weidemann for atomic systems [8], although we give a much simpler argument in the appendix for both atomic and molecular systems.

We begin the proof using fact 1 to choose the positive spectral point, $\lambda = \varepsilon^{1/2}$. Then using fact 2, we have that there exists an $x \in \mathrm{Dom}(H)$ of unit norm such that
$$0 \leqslant \|(H-\lambda)x\| = \left(H^2x, x\right) - 2\lambda(Hx, x) + \lambda^2 < \varepsilon = \lambda^2. \tag{2}$$

This gives

$$\bigl(H^2x, x\bigr) < 2\lambda(Hx, x). \tag{3}$$

Since H^2 is positive definite and $\lambda \neq 0$, we have

$$(Hx, x) = 0. \tag{4}$$

We save this result for later use.

We now *assume* that the bound eigenfunctions of H, ψ_n, form a complete orthonormal set (this is contrary to what we want to prove). Then we can write x as

$$x = \lim_{N\to\infty} x_N \quad \text{where } x_N = \sum_{n=1}^{N} c_n\psi_n. \tag{5}$$

For $M < N$, we have

$$\begin{aligned}\lim_{M,N\to\infty} \|Hx_N - Hx_M\| &= \lim_{M,N\to\infty} \left\| \sum_{n=M}^{N} c_n E_n \psi_n \right\| \\ &= \lim_{M,N\to\infty} \sum_{n=M}^{N} |c_n|^2 E_n^2 \leqslant B^2 \lim_{M,N\to\infty} \sum_{n=M}^{N} |c_n|^2 = 0,\end{aligned} \tag{6}$$

where B is a lower bound to lowest eigenvalue. This bound, B, always exists and can be taken as the hydrogenic eigenvalues summed according to the Pauli exclusion principle for atoms (lower bounds for molecules are functions of the lower bounds for atoms using the united atom theorem [7]). Alternate proofs of a lowest eigenvalue have been given in [4,5]. The sequence $\{Hx_n\}$ is thus Cauchy. Since Hilbert space is complete, all Cauchy sequences converge to some element. Fact 2 tells us that this element is Hx. We use this to show

$$\begin{aligned}&\lim_{N\to\infty} \bigl|(Hx, x) - (Hx_N, x_N)\bigr| \\ &\quad= \lim_{N\to\infty} \bigl|(Hx, x - x_N) + (Hx - Hx_N, x_N)\bigr| \\ &\quad\leqslant \lim_{N\to\infty} \bigl|(Hx, x - x_N)\bigr| + \lim_{N\to\infty} \bigl|(Hx - Hx_N, x_N)\bigr| \\ &\quad\leqslant \lim_{N\to\infty} \|Hx\| \cdot \|x - x_N\| + \lim_{N\to\infty} \|Hx - Hx_N\| \cdot \|x_N\| \\ &\quad\leqslant \|Hx\| \lim_{N\to\infty} \|x - x_N\| + \lim_{N\to\infty} \|Hx - Hx_N\| = 0.\end{aligned} \tag{7}$$

We thus have that

$$(Hx, x) = \lim_{N\to\infty} (Hx_N, x_N). \tag{8}$$

In the beginning, we showed that (Hx, x) is positive. Since (Hx_N, x_N) is the sum of negative numbers, it must be negative:

$$(Hx_N, x_N) = \sum_{i=1}^{N}\sum_{j=1}^{N}(Hc_i\psi_i, c_j\psi_j) = \sum_{i=1}^{N}\sum_{j=1}^{N}(E_ic_i\psi_i, c_j\psi_j) = \sum_{i=1}^{N} E_i|c_i|^2 < 0. \quad (9)$$

Since the limit of a sequence of negative numbers cannot be positive, we have a contradiction, indicating our assumption that there exists a complete set of eigenfunctions is incorrect. This is what we wanted to prove.

Appendix

The virial theorem for atomic and molecular systems in the Born–Oppenheimer approximation states that

$$2E_\mathrm{e} = -2(T\psi_\mathrm{e}, \psi_\mathrm{e}) = (V\psi_\mathrm{e}, \psi_\mathrm{e}) + \sum_\alpha q_\alpha \frac{\partial E_\mathrm{e}}{\partial q_\alpha}, \quad \text{(A.1)}$$

where E_e is the electronic energy, T is the electronic kinetic energy operator, V is the sum of the nuclear attraction and electron-electron repulsion operators, and ψ_e is any eigenfunction of the system [1]. The index α represents the nuclei and q_α the position of the αth nucleus.

For equilibrium nuclear configurations, the electronic energy is a local minimum and thus the partial derivative of the energy with respect to the nuclear coordinates is zero. This simplifies (A.1) to

$$2E_\mathrm{e} = -2(T\psi_\mathrm{e}, \psi_\mathrm{e}) = (V\psi_\mathrm{e}, \psi_\mathrm{e}). \quad \text{(A.2)}$$

Since (Tx, x) is always positive, the energy must always be negative. Thus, the set of eigenvalues is bounded above by zero and cannot include zero. That the set is bounded below has been proved separately by Kato [4] and Lieb [5]. So, although H is an unbounded operator, if it is restricted to the subspace spanned by its eigenfunctions, it becomes a bounded operator.

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