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1977 J. Phys. A: Math. Gen. 10 L91

(http://iopscience.iop.org/0305-4470/10/5/002)

J. Phys. A: Math. Gen., Vol. 10, No. 5, 1977. Printed in Great Britain.

LETTER TO THE EDITOR

The exponential decay of sub-continuum wavefunctions of two-electron atoms

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Received 28 January 1977, in final form 15 March 1977

Abstract. Progress on obtaining bounds on the exponential decay of sub-continuum atomic eigenfunctions is reviewed. A particularly simple bound is found for a sub-continuum eigenfunction of a two-electron atom. This bound is very natural, and it is shown to be essentially optimal. A generalization of this bound to an N-electron atom is suggested but not proved.

The subject of determining the correct asymptotic decay of bound eigenfunctions for atomic systems has received much attention. It is frequently thought that the proper asymptotic decay should be essentially that of $\exp[-(-2mE)^{1/2}\sum_{i=1}^{N} r_i/N^{1/2}]$ (Pekeris 1958, p 1649) or of $\exp[-(-2mE)^{1/2}(\sum_{i=1}^{N} r_i^2)^{1/2}]$ (Knirk 1974, p 77), where m is the electronic mass, E is the energy, and r_i is the distance of the ith electron from the nucleus, which is assumed to be infinitely massive. It is easy to see that a general bound of this type cannot exist for the solutions of Schrödinger's equation for multi-particle systems, for if such a bound did exist, negative-energy continuum states would be bounded by a decreasing exponential and hence would be square-integrable, a blatant contradiction.

A bound depending on r_1, r_2, and r_{12} was obtained for a sub-continuum eigenfunction of a three-particle system (Slaggie and Wichmann 1962, pp 959–60), and a bound has been found for a sub-continuum eigenfunction of a Hamiltonian whose pair potentials have Fourier transforms which are in L^1+L^q for some q in $[1, 2]$ (Simon 1974, p 399). Simon showed that for any θ in $(0, 1)$, the wavefunction is bounded by $K(\theta)\exp\{-\theta[2(E_c-E)]^{1/2}r\}$ where $r^2=\Sigma_i m_i\rho_i^2$ and E_c is the energy at the bottom of the continuum. The mass and the distance from the centre of mass of the ith particle are denoted by m_i and ρ_i, respectively.

One would be tempted to think that if a function F is an optimal bound in a particular limit, it ought to satisfy the differential equation in that limit. A recent study of the asymptotic behaviour of eigenfunctions of Hamiltonians with polynomially bounded potentials lends support to this belief (Simon 1975). In our case, we might expect TF/F to approach E in the limit as r_1, r_2, and r_{12} tend to infinity. Simon's bound does not satisfy this condition, for the appropriate limit of his bound is $E-E_c$. The physical explanation is easy to see, for Simon's bound is coarse; it does not distinguish between one electron tending to infinity and the other staying close to the nucleus and another situation in which both electrons tend to infinity at comparable rates.

Slaggie and Wichmann's bound, however, does satisfy the differential equation asymptotically, as can be verified by an extremely tedious computation. Nonetheless,

their bound is very cumbersome to use, and one would expect it to be extremely involved for an N-particle system. It has been suggested that a bound of the form

$$\exp\{-(2m)^{1/2}[(-E_c)^{1/2}r_1+(E_c-E)^{1/2}r_2]\}+\exp\{-(2m)^{1/2}[(E_c-E)^{1/2}r_1+(-E_c)^{1/2}r_2]\} \tag{1}$$

exists (Morgan 1976, p 20), and it has been argued that the asymptotic behaviour of the wavefunction for an He atom with an infinitely massive nucleus should be of this form (Fock 1954, pp 169–71, Ermolaev 1961, p 24). It will be noted that such a function asymptotically satisfies the differential equation, does not exceed Simon's bound, and ceases to be square-integrable if $E \geqslant E_c$. It is the purpose of this paper to demonstrate the existence of such a bound for a sub-continuum eigenfunction of a two-electron atom.

We shall study the function $F(x, y; b)$, which equals

$$[\exp(-px)+\exp(-x^2/z)]/[\exp(qy)+\exp(y^2/z)], \tag{2}$$

where $p^2+q^2=1$, $p=[(E-E_c)/E]^{1/2}=(1-b)^{1/2}$, $q=(E_c/E)^{1/2}=b^{1/2}$, and $z^2=x^2+y^2$ (Slaggie and Wichmann 1962, equation (95)). We have let $x=|\boldsymbol{x}|$ and $y=|\boldsymbol{y}|$. We note that we can let $p=\cos\gamma$, $q=\sin\gamma$, $x=z\cos\alpha$, and $y=z\sin\alpha$. If we can prove that $F(x, y; b)$ is not greater than a constant times $\exp(-px-qy)$, we shall have shown the existence of our bound (1).

We recall that if a, b, c, and d are positive real numbers, then $(a+b)/(c+d)\leqslant(a/c)+(b/d)$. Hence $F(x, y; b)\leqslant\exp(-px-qy)+\exp(-z)$. Furthermore, since $px+qy=z\cos(\gamma-\alpha)\leqslant z$, $F(x, y; b)\leqslant 2\exp(-px-qy)$.

To derive a simple bound for He eigenfunctions with arbitrary nuclear mass, we note that the third term in Slaggie and Wichmann's bound (equation (96)) is less than $2\exp(-z)$ since $|\boldsymbol{x}_3|/z\leqslant 1$. It should be noticed that the fact that two electrons cannot form a bound state, and hence that $b_3=0$, is absolutely critical in deriving this result. Thus we have shown that for every sub-continuum eigenfunction ψ of the He atom

$$|\psi(\boldsymbol{r}_1, \boldsymbol{r}_2)|\leqslant K(\theta)\{\exp[-\theta(px_1+qy_1)]+\exp[-\theta(px_2+qy_2)]\}, \tag{3}$$

for some constant $K(\theta)$, where $\boldsymbol{x}$ and $\boldsymbol{y}$ are defined on page 947 of Slaggie and Wichmann's paper and θ is in (0, 1).

We can see that our bound (3) is essentially optimal by comparing it with the exact wavefunctions for He with the inter-electronic repulsion 'turned off'.

The practical advantages of our bound over that of Slaggie and Wichmann are obvious. If the true wavefunction is approximated by

$$P(r_1, r_2, r_{12})\exp(-pr_1-qr_2)\pm P(r_2, r_1, r_{12})\exp(-qr_1-pr_2) \tag{4}$$

where P is a polynomial, the resulting integrals can be done in simple closed form.

To generalize this bound to an N-electron atom it is first necessary to construct a useful coordinate system. We denote by $\{\alpha_1, \alpha_2, \ldots, \alpha_N\}$ a permutation of $\{1, 2, \ldots, N\}$. We then let $\boldsymbol{\xi}_{\alpha_1}$ be the vector which joins particle α_1 with the centre of mass (CM) of the $\{\alpha_2, \ldots, \alpha_N\}$+nucleus system, $\boldsymbol{\xi}_{\alpha_2}$ be the vector which joins particle α_2 with the CM of the $\{\alpha_3, \ldots, \alpha_N\}$+nucleus system, etc. These coordinates enjoy the distinction that the kinetic energy in the CM system can be written as $\Sigma_i\,(P^2_{\alpha_i}/2\mu_{\alpha_i})$, where μ_{α_i} is the reduced mass for the α_i system (Messiah 1965). In this case $\mu_{\alpha_i}=m[(N-i)m+M][(N-i+1)m+M]^{-1}$, where m and M are the electronic and nuclear masses, respectively. These coordinates are an obvious generalization of those defined on page 947 of Slaggie and Wichmann's article.

We now let $\{E_1, E_2, \ldots, E_N\}$ be the ionization energies of the atom. We assume the convention that these numbers are positive. The generalization of our bound (3) to an N-electron atom would then seem to be a symmetrized sum of terms of the form

$$\exp\left(-\theta \sum_i [(2\mu_{\alpha_i} E_i)^{1/2} |\boldsymbol{\xi}_{\alpha_i}|]\right). \tag{5}$$

It is hoped that this bound can be derived directly.

It is a pleasure to thank E H Wichmann for numerous conversations on the subject of exponential decay. I would like to thank A O'Connor for referring me to the literature on this subject and B Simon for calling his 1975 paper to my attention. I am grateful to R A Harris for partial support made available under a grant from the National Science Foundation and to the University of California for granting me a fellowship.

Note added in proof. Inspired by a preliminary version of this article, Barry Simon, Percy Deift and Walter Hunziker have improved Simon's earlier results to yield a bound similar to (5) (B Simon, private communication).

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