$\{0.7712, 0.5572, 0, -0.5572, -0.7712\}$ and $\mathbf{f}'' = \{0.072, -0.443, -0.614, -0.443, -0.072\}$, which differ from the exact results by $\{-1.80, 0.36, 0, -0.36, 1.80\}$ % and $\{-, -1.4, 0.5, -1.4, -\}$ % respectively. By way of comparison, we note that the simpler approximations to $\mathbf{D}$ afforded by the use of only first or first and second differences (forward in the first three terms and backward in the last two) yield the much poorer approximations $\mathbf{f}'$ $\{0.707, 0.293, -0.293, -0.293, -0.707\}$ and $\mathbf{f}' = \{0.914, 0.586, -0.086, -0.586, -0.914\}$, respectively. In the use of only first differences, central differencing in all but the first and last rows generally would be preferable—*e.g.*,

$$h\mathbf{D} = \begin{bmatrix} -1 & 1 & 0 & 0 & 0 \\ -1/2 & 0 & -1/2 & 0 & 0 \\ 0 & -1/2 & 0 & -1/2 & 0 \\ 0 & 0 & -1/2 & 0 & -1/2 \\ 0 & 0 & 0 & -1 & 1 \end{bmatrix} \tag{25}$$

which yields $\mathbf{f}' = \{0.707, 0.500, 0, -0.500, -0.707\}$ for the above example.

NOTE ON THE MANY-PARTICLE PROBLEM*

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1. It was shown by Kato [1] that the symmetric Hamiltonian operator of every quantum mechanical system of particles, having a potential energy of the Coulomb type, is essentially self-adjoint; so that its closure, H, is self-adjoint (or, hypermaximal, in the terminology of von Neumann [4]). In [2], Kato applied this result to prove that the least point, λ_0, of the spectrum of H for the two-electron system is an eigenvalue, so that λ_0 lies in the point spectrum of H. The corresponding problem in the general many-electron system apparently still remains open. Thus, while the existence of a lower bound for the spectrum of H has been established (see [3], pp. 207–208; also [1], p. 205), no general criterion for the case of $N \geqq 3$ electrons guaranteeing that the least point of the spectrum is actually an eigenvalue (or, at least, no criterion which does not depend upon a variational procedure with the attending convergence questions) seems to be known. In this connection, see [3], pp. 196–197, also the remarks of Kato [2], p. 218, and the references cited there.

The object of this note is to point out that λ_0 must be an eigenvalue whenever the atomic number Z is sufficiently large. In fact, it will be shown that *the least point, λ_0, of the spectrum of the Hamiltonian operator, H, belonging to an atom with N electrons, atomic number Z, and a stationary nucleus, is in the point spectrum whenever*

$$Z \geqq 5N(N-1)/8. \tag{1}$$

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If $N = 2$, the inequality (1) is satisfied for all Z (where $Z = 2, 3, \cdots$); hence, as was already proved (and even more) in [2], λ_0 is an eigenvalue for every two-electron system. If $N = 3$, relation (1) is seen to hold for $Z \geqq 4$, thus including all three-electron ions except the lithium atom itself.

A point λ is said to be in the cluster spectrum of a self-adjoint operator $H = \int_{-\infty}^{\infty} \lambda dE(\lambda)$ if either λ is an eigenvalue with an infinite multiplicity or if every open interval about λ contains an infinity of values ($\neq \lambda$) belonging to the spectrum of H. In order to prove the italicized assertion, it is clearly sufficient to prove that $\lambda_0 < \mu_0$, where μ_0 denotes the least point of the cluster spectrum of H. (It is essentially this criterion which was verified by Kato [2] for the two-electron system.)

2. The wave equation for the N-electron system is given by $H\phi = \lambda\phi$ where the Hamiltonian H is defined, for a proper choice of units, by

$$H = \sum_{k=1}^{N} (-\nabla_k^2 - 2Z/r_k) + \sum_{1 \leq j < k \leq N} 2/r_{jk} . \tag{2}$$

That H is self-adjoint was proved in [1]. Since the eigenvalues of each hydrogenlike Hamiltonian $H_k = -\nabla_k^2 - 2Z/r_k$ are given by $-Z^2/n^2$ ($n = 1, 2, \cdots$), and since the operator corresponding to the second summation of (2) is non-negative, it is clear that the least point, μ_0, of the cluster spectrum of H satisfies

$$\mu_0 \geqq -(N - 1)Z^2; \tag{3}$$

see [2], p. 216 for the case $N = 2$.

Next, let ϕ_k denote the (real-valued) normalized eigenfunction belonging to the ground state of the system with Hamiltonian H_k and define the (normalized) function ϕ by $\phi = \prod_{k=1}^{N} \phi_k$. In view of the evaluations

$$2 \iint [(\phi_j\phi_k)^2/r_{jk}] \, dv_j \, dv_k = 5Z/4, \tag{4}$$

the contribution of each of the $N(N - 1)/2$ terms $2/r_{jk}$ occurring in (2) to the inner product $(H\phi, \phi)$ is $5Z/4$. (The integrals (4) occur in first order perturbation theory; see e.g., [5], pp. 163–164 for the case of the helium atom.) Consequently,

$$\lambda_0 \leqq (H\phi, \phi) = -NZ^2 + 5N(N - 1)Z/8. \tag{5}$$

If, in (5), $\lambda_0 = (H\phi, \phi)$, then obviously λ_0 is an eigenvalue. Suppose then that $\lambda_0 < (H\phi, \phi)$. As was remarked earlier, λ_0 is in the point spectrum of H whenever $\lambda_0 < \mu_0$. In view of (3) and (5), this inequality is impleid by (1), so that the proof of the italicized assertion is now complete.

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