[5] P. Lindner, Int. J. Quantum Chem. **4,** 217 (1970).
[6] M. H. Alexander, Phys. Rev. **A1,** 1397 (1970).
[7] R. E. Johnson, S. T. Epstein and W. J. Meath, J. Chem. Phys. **47,** 1271 (1967).
[8] A. Dalgarno, Advan. Phys. **11,** 281 (1962).
[9] W. Kolos, Int. J. Quantum Chem. **1,** 169 (1967).

Received September 27, 1971.

New Proof of the Minimum Principle for Excited States

RALPH H. YOUNG*

Department of Chemistry, University of California, Riverside, California 92502, USA

Let H be a self-adjoint operator in Hilbert space. It is a well-known and frequently used fact that the nth root of a linear variational computation for H is an upper bound to the nth eigenvalue of H [1, 2, 3]. The invariably cited references [1] are incomplete in that they neglect questions of convergence for their sequence of successive approximations. Complete proofs have been based on maximum-of-minima arguments [2] or repeated application of the Rayleigh–Ritz principle [3]. Here is an alternative proof, which hopefully sheds additional light on the nature of this upper-bound principle.

Let $f_1, f_2, \cdots, f_n$ be n functions such that

$$\left.\begin{aligned}\langle f_i | f_j\rangle &= \delta_{ij}\\ \langle f_i| H | f_j\rangle &= \tilde{E}_i\,\delta_{ij}\end{aligned}\right\}\quad \text{for}\quad i, j = 1, 2, \cdots, n \tag{1}$$

(These may be the first n solutions to a linear variational problem.) We assume that H has a purely discrete spectrum from $-\infty$ *past* $\tilde{E}_n$ (i.e. on $(-\infty, \tilde{E}_n + \epsilon]$ for some $\epsilon > 0$); let the $\psi_k (k = 1, 2 \cdots)$ be the orthonormal eigenfunctions of H corresponding to eigenvalues $E_k \leqq \tilde{E}_n$. We wish to prove that there are at least n such ψ_k's; or, equivalently, that the manifold $\mathscr{M}_\psi$ spanned by these eigenfunctions has dimension $\geq n$.

The manifold spanned by the f_k's, $\mathscr{M}_f$, resembles $\mathscr{M}_\psi$ in that

$$\langle g| H |g\rangle \leqq \tilde{E}_n \|g\|^2 \quad \text{if} \quad g \in \mathscr{M}_f \tag{2}$$

It seems unreasonable that $\mathscr{M}_\psi$ should have smaller dimension than $\mathscr{M}_f$. To confirm

* Present address: Eastman Kodak Research Laboratories, Rochester, New York 14650, U.S.A.

this suspicion, we show that the n functions Pf_k,

$$Pf_k = \sum_{E_j \leqq \tilde{E}_n} \langle \psi_j \mid f_k \rangle \psi_j \tag{3}$$

which clearly are in $\mathcal{M}_\psi$, are linearly independent. (P is the projector onto $\mathcal{M}_\psi$.) Were they not, there would be a choice of coefficients a_k, not all zero, such that

$$\sum_{k=1}^{n} a_k(Pf_k) = 0 \tag{4}$$

$$\sum_{k=1}^{n} a_k f_k = (1 - P) \sum_{k=1}^{n} a_k f_k \tag{5}$$

in which case

$$\begin{aligned} \left\langle \sum_{k=1}^{n} a_k f_k \middle| H \middle| \sum_{k=1}^{n} a_k f_k \right\rangle &= \left\langle (1 - P) \sum_{k=1}^{n} a_k f_k \middle| H \middle| (1 - P) \sum_{k=1}^{n} a_k f_k \right\rangle \\ &> \tilde{E}_n \left\| (1 - P) \sum_{k=1}^{n} a_k f_k \right\|^2 \\ &= \tilde{E}_n \left\| \sum_{k=1}^{n} a_k f_k \right\|^2 \end{aligned} \tag{6}$$

Equation (6) contradicts (2), since $\sum_{k=1}^{n} a_k f_k \in \mathcal{M}_\psi$. Hence $\mathcal{M}_\psi$ has dimension $\geq n$, H has at least n eigenvalues $\leqq \tilde{E}_n$ (counting m-fold degenerate eigenvalues m times), and

$$E_n \leqq \tilde{E}_n \tag{7}$$

Acknowledgement

The author wishes to thank Dr. Walter J. Deal and Dr. William H. Miller for helpful conversations on this subject, and the referee for an additional reference.

Bibliography

[1] E. A. Hylleraas and B. Undheim, Z. Physik. **65,** 759 (1930); J. K. L. MacDonald, Phys. Rev. **43,** 830 (1933).
[2] S. H. Gould, *Variational Methods for Eigenvalue Problems* (University of Toronto Press, Toronto, 1957); J. F. Perkins, J. Chem. Phys. **45,** 2156 (1966).
[3] P.-O. Löwdin, Phys. Rev. **139,** A357 (1965).

Received March 11, 1971
Revised September 20, 1971