the other hand there is no independent way; to get them one must have essentially the exact many electron function ψ to start with.

The orbitals obtained by adding the further $\hat{f}_i$ to the H.F. orbitals approach the generalized SCF orbitals i_G. They are also close to the first natural spin orbitals i_{nso} as shown by Davidson and Jones.[11]

$$i_G \cong \frac{i_{\text{H.F.}} + \hat{f}_i}{(1 + \langle \hat{f}_i, \hat{f}_i \rangle)^{\frac{1}{2}}} \cong i_{\text{nso}} . \tag{17}$$

Their calculations on the ground state of H_2 at the equilibrium distance showed the first natural orbital to be very close to the Hartree–Fock orbital.

CONCLUSION

A method has been given which shows how a many electron trial function $\tilde{\psi}$ of arbitrary functional form and many parameters can be analyzed into physically and chemically meaningful terms and improved by the examination of these terms. It is also shown how from a trial $\tilde{\psi}$ which bypasses the Hartree–Fock method, the Hartree–Fock orbitals can be obtained just by partial integrations without requiring a separate variational calculation.

Discussion on Atomic Spectra

J. C. SLATER, *Chairman*

MURRELL: Can anything further be deduced from Rydberg defects for molecules concerning the effects of penetration or polarization?

MACK: Edlén's forthcoming *Handbuch der Physik* monograph has a pertinent discussion.

HORAK: Some years ago, I made calculations of x-ray states like $1s(2s)^2(2p)^6\ ^2S$ using the Morse–Young–Haurwitz analytical wave functions (Z. Horak, Czech. J. Phys. **8**, 271, 1958). In connection with this research an interesting problem arose.

The question is: If you apply the variational principle, you have to orthogonalize—as everybody suggests—to lower lying states of the same symmetry. But what to do here? Let's analyze what we do in practice. We forget about our "orthogonality catastrophe" and look simply for the extremum of the variational functional, $\delta \int \psi^* H \psi d\tau$. No doubt, such extremes exist; this means also that the extremization should be useful even for ordinary excited states like $(1s2s)\ ^1S$, which was actually the case. Evidently in the case of extremization the advantage of the variation principle $E \geqslant E_{\text{exact}}$ is now lost.

The question is: why don't we substitute in atoms the variation principle by the Z perturbation expansion? Especially in x spectra, everybody knows that the Moseley-like formulas of the type $1/n^2\ (Z - S)^2$ or simply three-term formulas $aZ^2 + bZ + c$ fit the experimental data very well. The problem is in the calculation of c, but if we start with the second-order perturbation formula $\sum_j [|H_{ij}|^2/(E_i - E_j)]$ (including the continuum), we can calculate energy differences directly. We thus avoid taking small differences between two big quantities as the HF-method does (a particularly outstanding feature in x-ray spectra) a procedure which Professor Coulson characterized as "weighing of the captain of the ship by weighing the ship when he is or is not on board."

LÖWDIN: Just a word of warning from the mathematical side: orthogonality $\langle \varphi_k | \varphi_l \rangle = 0$ is not sufficient to ensure the existence of an upper bound to the energy; one needs also the noninteraction property $\langle \varphi_k | H | \varphi_l \rangle = 0$.

MCWEENY: In some recent work [R. McWeeny and Y. Öhrn, Technical Report, No. 60, 15 Feb. 1961, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished)], Yngve Öhrn and I investigated systems with a single-series electron, using an approximate wave function

$$\Psi(1,2,\cdots N) = \mathcal{A}[\Phi(1,2,\cdots N-1)\varphi(N)] .$$

Here Φ is an arbitrary wave function (possibly an exact wave function for the positive ion), φ describes the series electron, and $\mathcal{A}$ is an antisymmetrizer. It is then possible to formulate a one-body eigenvalue equation to determine φ, all core penetration effects (including nonorthogonality) being absorbed into an effective one-body Hamiltonian, containing certain pseudopotentials which ensure that a variational φ will not "collapse" into the core. The energy of the whole system is then $E = E_{\text{core}} + E_{\text{series}}$ and if E_{core} is sensibly constant for different series electron states

the series electron spectrum follows directly from the one-body equation: variational calculations on this equation then permit the discussion of quantum defects, etc., in terms of the core potentials. Preliminary applications to lithium and sodium, using Slater-type functions, have been completed: a calculation on lithium with a Hylleraas-type core function is in progress.

SINANOĞLU: The variation–perturbation method for excited states [Oktay Sinanoğlu, Phys. Rev. **122**, 491 (1961)] may allow one to use the minimum principle even for $(2s^2)\ ^1S$. The trial function $\psi(\mathbf{x}_1\mathbf{x}_2,)$ is made orthogonal to an average $1s$ orbital

$$\int \psi(\mathbf{x}_1,\mathbf{x}_2)\varphi(\mathbf{x}_1)d\mathbf{x}_1 = 0\,.$$

This keeps ψ orthogonal to the infinity of "unperturbed" states $1s^2$, $1s2s,\cdots,1s\infty s$.

In series levels, the correlation energy between the outer electron and the core may be calculated by the "core-polarization" method. This refers to the *instantaneous* polarization of the core by the slower outer electron, and this theory is available including penetration effects, etc. [Oktay Sinanoğlu, J. Chem. Phys. **32**, 1212 (1960)]. The "core-polarization potential" is the same for all the outer electron orbits. The effects of the outer electron on the core energy itself have also been stated and estimated for Li and Li_2.

LÖWDIN: Dr. Holøien in Oslo has made a very interesting study of the state $(2s)^2$ in the series of He-like ions in comparison to the series of states $(1sns)$ for $n = 1, 2, 3,\cdots\infty$. He points that one gets a good approximation to the $(2s)^2$ energy with a secular equation of a rather low order, and that the $(2sns)n \geqslant 2$ series "starts out" long before the $(1sns)$ series is finished. In this connection, he emphasizes the problem of defining the $(2sns)$ states $(n \geqslant 2)$ properly in view of the fact that all these states should be orthogonal (and noninteracting) with the infinite series of states $(1s, ns)$, $n = 1, 2, 3,\cdots\infty$.

One possible solution may be provided by considering the dominant term in the "natural expansion" and classify the orbitals occurring by their symmetry and the number of their nodal surfaces.

NESBET: Have the previous speakers taken into account the polarization potential felt by the series electron? This is an instantaneous correlation effect, so it can't be represented by a wave function in which the inner shell is frozen, independent of n for the series electron. In work on the theory of electron scattering using the nuclear-optical model (by C. E. Porter and collaborators at Brookhaven), the polarization potential, which is a long range potential, has an important effect on the low-energy cross section.

MCWEENY: There is convincing evidence that the core energy is not sensitive to changes in state of the series electron. For example, the early work by James showed that the lithium core function was scarcely modified even by complete removal of the valence electron, to leave the positive ion.

JAMES: I agree; on the whole it does seem as if correlation between core and outer electron may be neglected.

SCHERR: In connection with Löwdin's remarks concerning doubly ionized states of the He atom that lie in the continuum, I would like to call your attention to a (probably) unpublished note by Dr. U. Fano (N.B.S.) in which he accounts for the line shape of such a line—$2s^2$ in the continuum—observed by Lassiter at Ohio. I believe preprints are available.

MACK: I should like to emphasize that the (presumed Li II) lines Herzberg and Moore list as unclassified are sharp lines, even showing hyperfine structure, to the red of the $(1sns)$ series limit, and experimentally indistinguishable, so far as I know, from the usual lines between discrete states.

SLATER: This might be a suitable time to mention the work of Professor Shenstone, who is not here, but has celebrated his 70th birthday this past year. He pointed out, many years ago, the configuration interaction occurring when a discrete level of one type is inserted into a sequence of the discrete levels of another type.