Discussion on Electronic Structure of Atoms

L. C. GREEN, *Chairman*

HYLLERAAS: I felt much indebted to the article by J. C. Slater [Proc. Nat. Acad. Sci. **13**, 423 (1927)] which is cited in two of my articles (1928 and 1929). Even though I could not make direct use of Slater's article, it might well have contributed to my final choice of wave function. I do not remember another article by Slater in the *Physical Review* in which the coordinate r_{12} had already been used in an exponential function.

In my article of 1929 I started with exponential functions like $\exp(cr_{12})$ and was rather surprised to find that the more convenient expression $(1 + cr_{12})$ proved even more successful.

HIRSCHFELDER: Do you know of any work going on as to the preparation of tables of screening constants for properties other than energy?

SLATER: Exponential wave functions are not very accurate in any case. Rather than putting extra effort into their elaboration, I should prefer to see the effort put into determination of more accurate wave functions and find average values from them.

DALGARNO: On the use of screening constants for estimating atomic properties other than the eigenvalue; the use of Slater's screening constants implies that

$$E = a(Z - s)^2 = aZ^2 - 2asZ + as^2 \tag{1}$$

is a good approximation to the eigenvalue E. The correct form of E can always be put in the form

$$E = a(Z - s)^2 + bZ + c + \frac{d}{Z} + \cdots \tag{2}$$

and an atomic property can be written similarly

$$P = \alpha Z^n + \beta Z^{n-1} + \gamma Z^{n-2} + \cdots . \tag{3}$$

Comparing (1) and (2) suggests replacing (3) by

$$P = \alpha(Z - S_p)^n , \tag{4}$$

where

$$S_p = -\beta/\alpha n \tag{5}$$

is a screening constant which depends not only on the atomic system but also on the property under consideration. This procedure is described in a paper by A. Dalgarno and A. L. Stewart [Proc. Roy. Soc. (London) **A257**, 354 (1960)].

NESBET: E. Clementi, using Roothaan's programs, at IBM, San Jose, is producing analytic Hartree–Fock functions by mass production, working down through the periodic table. As a byproduct, he has obtained best single-exponent sets (analogous to Slater orbitals, but determined variationally) through Kr.

GILBERT: (This contribution appears at the end of the discussion on Slater's paper.)

MATSEN: If one wishes, by configuration interaction, to obtain ground state energies better than those obtained by extended-basis-self-consistent-field calculations, will these self-consistent-field orbitals be useful in the construction of the excited configurations?

SLATER: The experience of many workers, particularly of Dr. Louis Green, shows that the use of the excited self-consistent orbitals gives a much slower convergence than the use of orbitals constructed more like those used by Hylleraas in his original helium work, not extending out to such large radii.

COLEMAN: W. Conkie (Physics Department of Queen's University, Kinston) will report at The American Physical Society meeting on 25 January 1963, his work on calculating the ground state energy of Li and Be^+. He uses an analytic variational procedure with an ansatz motivated by the density matrix approach. Using Hylleraas-type terms for correlation between the two 1*s* electrons, he obtains 0.03% accuracy for Be^+ and considerably better for Li.

HORAK: The approximation of atomic energies in terms of Z, mentioned by Dalgarno, W

$= aZ^2 + bZ + c + \cdots$ can be treated by the Schrödinger perturbation theory. For c we have the sum $c = S[|H_{0i}|^2/(E_0 - E_i)]$ where S represents summation over all discrete and continuum states. For example, for helium $(1s)^2\ ^1S$ the series consists of contributions from

$$1s\,ns\ ^1S\,, \qquad nl\,n'l'\ ^1S\,,$$
$$1s\,Es\ ^1S\,, \qquad El\,E'l'\ ^1S\,.$$

Corresponding calculations for $(1s)^2\ ^1S$ were carried out by Scherr. The above-mentioned formula for c has the advantage that we are able to calculate directly differences of atomic energies, which are always of practical importance. Once we have separated the single substitution part—in fact, Dr. M. N. Lewis at Harvard College Observatory wrote a program for the IBM 7090, which is capable of doing this for any first row atom—we find that the double substitution terms which contribute to c are the same in many cases. As an example, the sum corresponding to $(1s)^2 \rightarrow nln'l$, $El\,E'l$ will be the same both for $(1s)^2(2s)^2\ ^1S$ and $(1s)^2(2s)^2(2p)^6\ ^1S$, except that the Pauli principle does not allow $(1s)^2 \rightarrow (2s)^2$ or $(1s)^2 \rightarrow (2p)^2$ (which can be subtracted easily from the whole sum). As pointed out by Sinanoğlu, we can, in a similar way, build up correlation energies from the corresponding pair interactions. As a matter of fact, for some special examples of atomic energy differences, we are able to exclude the double sums completely and express the corresponding c as a single running index sum, which our program is able to compute.

SINANOĞLU: 1. In a wave function such as

$$\varphi_0(1 + \alpha r_{12})$$

for He, the second term is not just the correlation part even if φ_0 is the H.F. (Hartree–Fock) wave function; it still includes some φ_0.

Better insight into correlation can be obtained by rewriting a wave function ψ after a change of normalization as

$$\psi = \varphi_0 + \chi\,, \quad \text{where} \quad \langle\varphi_0|\chi\rangle = 0\,, \tag{1}$$

and φ_0 is the H.F. wave function.

With the Hylleraas six-term wave function for He

$$\langle\psi|\psi\rangle = 1 + \langle\chi|\chi\rangle = 1.0075 \tag{2}$$

$\langle\chi|\chi\rangle$ is a measure of relative energy effects useful qualitatively in larger systems.

χ may be graphed to show the true correlation part of the electronic motion.

2. There has been a tendency to think in terms of either C.I. (configuration interaction) or r_{12} methods even for many-electron systems. Each method has strong limitations by itself, e.g., the usual difficult integrals come up if an r_{ij} is introduced for each pair of electrons (Szasz).

Even within a single N-electron system, however, there are different types of pair correlations. "Many-electron theory" [Oktay Sinanoğlu, J. Chem. Phys. **36**, 706, 3198 (1962)] allows a different method to be used for each type of pair, e.g., the r_{12}—method for $1s^2$, "core-polarization" for $1s2s$, "first-order C.I." for $2s^2$ in Be, SPO (split p-orbital) method for $(2p_z)^2$ in Ne, etc. The procedure is practical and systematic even for large systems.

3. "Many-electron theory" shows that

$$E \leqslant E_{\text{H.F.}} + \sum_{i>j}^{N} \varepsilon_{ij} + R\,, \tag{3}$$

where ε_{ij} are variational pair correlations separately minimized. R involves mainly 3-electron correlations; it is estimated as a minor correction using the pair functions. In most atoms and molecules

$$E \simeq E_{\text{H.F.}} + \sum_{i>j}^{N} \varepsilon_{ij}\,; \tag{4}$$

this predicted additivity was recently confirmed by the empirical results of E. Clementi and later by Allen and his collaborators, on the first row atoms.

The sum in Eq. (4) includes the *inter*-shell pairs (these give rise to Van der Waals attractions in molecules).

J. Linderberg and H. Shull [J. Mol. Spectr. **5**, 1 (1960)] found the $(2s)^2$ correlation, ε_{34} to be proportional to Z in the $(1s^2 2s^2)$ Be isoelectronic series. This arose from the strong $2s^2$–$2p^2$ mixing.

The empirical results show this linearity in Z for the neutral *atoms* Be, $B_1 \cdots$Ne as well.

The "exclusion effect"

$$\langle U_{ij}|K\rangle = 0$$

in "Many-Electron Theory" shows, however, that with added $2p$ electrons, the $2p^2$ mixing in ε_{34} is reduced from about 1.3 eV in Be to 0.8 eV in B, 0.5 eV in C down to zero in $N(^4S)$ through Ne.

Either the empirical data needs reexamination or else there is an unexpected increase in the rest of ε_{34} with Z. (V. McKay and I at Yale are looking into the problem.)

DONATH: Boys, as well as I, have made calculations for F^-, Ne, and Na^+. These showed that there was appreciable correlation between $2s$ and $2p$ electrons. This contribution was about 0.05 to 0.1 a.u. Total correlation energy is about 0.4 a.u.

DALGARNO: Sinanğolu has asserted that the Hartree–Fock approximation is the best starting point for an accurate calculation. Taking best to be in the sense of the greatest accuracy for the least labor, his statement is incorrect. Other starting points, such as the screened hydrogenic approximation (there are many other possibilities) may be dealt with more completely and lead to greater accuracy more easily. It will depend upon the particular property under consideration. For example, in the calculation of the mass-polarization corrections in the beryllium sequence, the Hartree–Fock approximation is a poor starting point which yields an answer of zero. The screened hydrogenic approximation is immediately superior.

SHERR: When one works with an isoelectronic series for an atomic wave function, it is possible to recover numbers which, in principle, are constants independent of Z. For example, from ordinary Schrödinger perturbation theory for the N-electron atom, it is known that

$$\psi(Z) = \sum_n Z^{-n}\psi_n .$$

Thus, from

$$\langle\Omega\rangle = \int d\tau\psi^*\Omega\psi ,$$

where Ω is any operator, it follows that one may write

$$\langle\Omega\rangle = \sum_n Z^{a-n}\Omega_n ,$$

where Ω_n are numbers independent of Z, and a is some known integer. Since one has only approximate wave functions, Ω_n recovered from them [C. W. Scherr, J. N. Silverman, and F. A. Matsen, Phys. Rev. **127**, 830 (1962); C. W. Scherr and J. N. Silverman, J. Chem. Phys. **37**, 1154 (1962)] are obtained as average values with a concomitant mean-square spread, σ_n^2. The σ_n^2, of course, are functions of the parameters in the wave functions. It is plausible to expect that if a σ_n^2 were zero (as well as all σ_m^2, $m < n$), then the correct value of the corresponding Ω_n would have been obtained. Thus, if the parameters are varied, consistently with maintaining $\sigma_m^2 = 0, m < n$, *a variational procedure which does not invoke the Hamiltonian* is established. Further, the procedure obtains the best wave function to a given order, of a given class of wave functions, specifically for the particular property of interest. It is probably necessary, in any event convenient, to write the parameter that is being varied, λ, in the form $\lambda_0 Z^a$ where a is a known—but not necessarily integer—number depending on the nature of λ. Thus, if λ is a scale factor, $a = 1$.

Many variants are possible. Cohen and Dalgarno [M. Cohen and A. Dalgarno, Proc. Roy. Soc. (London) **A261**, 565 (1961)] for example, choose their scale factor for an isoelectronic series by requiring it to reproduce a known Ω_1 value exactly.

It is planned to start a numerical investigation shortly.