differentiation of *P. pestis* and *P. pseudotuberculosis* than did D_T . These two species are very closely related taxonomically but *P. pestis* has a slower growth rate; thus differentiation of the two species may be entirely on the basis of vigour. Similarly, a limited analysis of different incubation temperatures for sugar fermentation by *Staphylococcus aureus* showed that the observed differences could be attributed to vigour differences. Perhaps the most important point raised by the analysis of a group of chromobacteria was to stress that the vigour concept has its major usefulness within a close taxonomic group. A very striking result was the low vigour of *Pseudomonas iodinium*, a species which grows quite fast but is rather inactive, at least on the evidence of the tests made. The data on this bacterium only re-emphasized the difficulty which surrounds its taxonomy. Conversely, the use of D_P or S_P seems promising for analyses of distantly related organisms. Apart from their deployment in taxonomic studies, Sneath suggests that the new coefficients could have application in such fields as medical diagnosis and ecology "where qualitative characters may be heavily dependent on factors involving abundance or time".

QUANTUM MECHANICS

Calculating Bounds for Overlap

from a Correspondent

QUANTUM mechanical calculations for interacting electrons in atoms, molecules and solids still present great difficulties when a careful inclusion of electron interactions is necessary. For a long time, attention was focused on approximating to the ground state energy, and it is well known that an upper bound to this energy can be obtained by averaging the Hamiltonian H of the system with respect to a normalized but approximate representation of the ground state wave function. This average is stationary with respect to small variations from the exact ground state and is therefore to some extent insensitive to the choice of trial wave function, which means that a very useful approximation to the ground state energy can be obtained with a relatively poor wave function.

Ways of calculating quantities other than the ground state energy from such inequalities have been of interest for some time. The early work of Eckart¹ is, for example, interesting, although it has not so far been widely used. The subject has been reopened recently by Weinhold who, in a series of papers²⁻⁴, has considered the overlap between wave functions and also the quantum mechanical averages of positive operators such as the Coulomb interaction energy e^2/r_{12} between two electrons separated by distance r_{12} . The method is sufficiently interesting to be worth developing in certain specific cases. We start with the discussion of the overlap between two approximations, say, φ_1 and φ_2 , to the exact wave function ψ . If we define the overlaps between these wave functions by the equations

$$S_1 = \langle \varphi_1 | \psi \rangle, S_2 = \langle \varphi_2 | \psi \rangle \text{ and } S_{12} = \langle \varphi_1 | \varphi_2 \rangle$$

and suppose these are non-negative and real, then if values of, say, S_2 and S_{12} are known, the strongest requirement that can be placed on the overlap S_1 is that the Gram matrix S of the normalized wave functions $|\varphi_1\rangle$, $|\varphi_2\rangle$ and $|\psi\rangle$ must be positive semi-definite, as shown, for example, by Mirsky⁵. This

leads to a quadratic equation which gives for the minimum value of S_1 the result

$$\langle \varphi_1 | \psi \rangle \geq \text{Min} \{S_1\} = S_2 S_{12} - [(1 - S_2^2)(1 - S_{12}^2)]^{1/2} \quad (1)$$

Differentiating this to get

$$\frac{\delta S_1}{\delta S_2} = S_{12} + S_2 \left[\frac{1 - S_{12}^2}{1 - S_2^2} \right]^{1/2} > S_{12} \quad (2)$$

we can say that because the derivative is positive the inequality in equation (1) will remain rigorously valid so long as S_2 is itself a lower bound.

In the work of Eckart referred to here¹ a crude lower bound for the overlap of a trial function φ with wave function ψ is given by

$$\langle \varphi | \psi \rangle > \left\{ 1 - \left[\frac{\varepsilon - E_0}{E_1 - E_0} \right] \right\}^{1/2}$$

where ε is the quantum mechanical average of H with the trial wave function φ while E_0 and E_1 are energies of the ground and the first excited state of the same symmetry for the exact Hamiltonian. Of course, in general E_1 and E_0 are not known, but they can be obtained experimentally. Taking the beryllium atom with four electrons as an example, the above method shows that the Hartree-Fock wave function has an overlap with the exact ground state wave function greater than 0.880 whereas the criterion of Eckart applied directly gives 0.79. If the Hartree-Fock wave function had been exact the overlap would naturally have been unity.

More recently, Weinhold has shown how this procedure has been applied to calculate quantum mechanical averages of an operator $F \geq 0$. If we denote by $\langle F \rangle$ the average $\langle \varphi | F | \varphi \rangle$ and use the notation

$$(\Delta F)^2 = \langle F^2 \rangle - \langle F \rangle^2,$$

then the interesting result obtained by Weinhold for the average of F is that

$$\langle \varphi | F | \psi \rangle \geq \{S \langle F \rangle - \Delta F (1 - S^2)^{1/2}\} / \langle F \rangle$$

It is usually not too difficult to calculate the quantities involved and so to obtain approximations to physically interesting quantities, such as the average of r^2 in an atom related to the diamagnetic susceptibility, or the inter-electronic repulsion in helium related to the average of e^2/r_{12} mentioned here. Once again, the above inequality follows from the non-negativity of the Gram determinant of the vectors $|\psi\rangle$, $|\varphi\rangle$ and $F|\varphi\rangle$. This result, moreover, can always be improved if the averages of FH and H^2 can be got by enlarging the Gram determinant to include the vector $H|\varphi\rangle$. Applications include the calculation of useful lower bounds for inter-electronic energies and for diamagnetic shielding. Although the method looks promising in some circumstances, one has to be careful because the bounds obtained for some positive definite operators are sometimes bad. Clearly, however, the method has some power and may eventually be a valuable additional tool in tackling the problem of correlated motions of electrons, especially in small atoms and molecules.

¹ Eckart, C., *Phys. Rev.*, **36**, 878 (1930).

² Weinhold, F., *J. Chem. Phys.*, **46**, 2448 (1967).

³ Weinhold, F., *J. Phys. A (Proc. Phys. Soc.)*, **1**, 305 (1968).

⁴ Weinhold, F., *J. Phys. A (Proc. Phys. Soc.)*, **1**, 535 (1968).

⁵ Mirsky, L., *Introduction to Linear Algebra*, 423 (1955).