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Quantum-Mechanical Kinetic Energy Transformation[*][†]

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It is shown that by a transformation of the usual expression for the kinetic energy matrix elements a simpler formula results which yields, for numerical wave functions, higher numerical accuracy for the kinetic energy than has previously been obtained. The derivation of the transformation and the numerical results of several applications are presented.

IN the one-electron approximation to solutions of the many-electron problem, accurate one-electron wave functions are necessary if reasonably accurate results are to be achieved. For problems involving the properties of molecules and solids it is common to use as basis, sums of products of suitable linear combinations of a set of atomic functions which are accurate solutions of the Schrödinger equation for the free atom. As is well known, the "best" set of free atom wave functions are those found as self-consistent field (SCF) solutions of the Hartree-Fock equations. However, as these wave functions are tabulated to three decimal figures only, it is not easy to overcome the difficulties associated with calculating total energies. This is particularly true in calculating matrix elements of the kinetic energy operator because the radial parts of the SCF wave functions are usually rapidly varying and so are more difficult to differentiate numerically.

It is the purpose of this note to show that by a transformation of the usual kinetic energy expression, a simpler formula results which yields a higher accuracy than has heretofore been obtained.

The kinetic energy matrix elements K. E. are defined by the expression

$$\text{K.E.} = -\int \varphi_1^*(\mathbf{r})\nabla^2\varphi_2(\mathbf{r})dv, \tag{1}$$

where φ_1 and φ_2 are any two one-electron wave functions and ∇^2 is the ordinary Laplacian operator in spherical coordinates. In our applications the φ's are Hartree-Fock atomic functions; the method itself, however, is valid for any set of wave functions.

The numerical calculation of kinetic energies using Eq. (1) yields poor results because even though the Hartree-Fock radial functions are smooth, they are rapidly varying functions and hence their first derivatives and more especially their second derivatives, which enter through the Laplacian, are not smooth, thereby introducing numerical errors into the results. By using Green's theorem Eq. (1) may be transformed into

$$\text{K.E.} = \int \nabla\varphi_1^*(\mathbf{r})\cdot\nabla\varphi_2(\mathbf{r})dv, \tag{2}$$

with ∇ the gradient operator. After performing the angular integrations in Eq. (2), the resulting equation is

$$\text{K.E.} = \int_0^\infty \left[\frac{dP_1}{dr}\cdot\frac{dP_2}{dr} + \frac{l(l+1)}{r^2}P_1P_2\right]dr, \tag{3}$$

where $P_i(r)$ denotes r times the radial part of φ_i and l is the ordinary angular momentum quantum number. The advantage of circumventing the use of Eq. (1) and its associated difficulty in attaining numerical accuracy has led to a widespread use of Eq. (3).

The results obtained from Eq. (3), although much better than those obtained from Eq. (1) are not as accurate as we wish; kinetic energy integrals still represent the most inaccurate part of the numerical calculations. This is particularly true for the wave functions of zero angular momentum as they are most rapidly varying at small values of the radial distance r, where the tabulated SCF wave functions are usually given to too few significant figures.

We shall now show that by a transformation of the P functions most of these difficulties may be removed. Letting $P = u\psi$, where u is an arbitrary function, and denoting the derivative with respect to r by the prime, we obtain

$$\begin{aligned}
P_1'P_2' + \frac{l(l+1)}{r^2}P_1P_2
&= u^2\psi_1'\psi_2' + uu'\psi_1'\psi_2 + uu'\psi_1\psi_2' \\
&\qquad + (u')^2\psi_1\psi_2 + \frac{l(l+1)}{r^2}u^2\psi_1\psi_2 \\
&= u^2\psi_1'\psi_2' + \frac{d}{dr}(uu'\psi_1\psi_2) + \left(\frac{l(l+1)}{r^2} - \frac{u''}{u}\right)u^2\psi_1\psi_2.
\end{aligned}$$

The equation $l(l+1)/r^2 - u''/u = 0$ has the solutions, $u = r^{l+1}$ and $u = r^{-l}$. The former is numerically useful

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for the functions $P(r)$ under consideration, since the boundary condition $P(0)=0$ implies that P/r^{l+1} remains finite at $r=0$.

Substituting $P=r^{l+1}$ into Eq. (3) and carrying out the integration, we have the final result that the kinetic energy matrix elements equal

$$\text{K.E.}=\int_0^\infty \frac{d\psi_1}{dr}\frac{d\psi_2}{dr}r^{2l+2}dr. \tag{4}$$

The advantage of using Eq. (4) is now immediately apparent. First of all, a calculational simplification results by having reduced the number of terms in the formula. Next, since the function $\psi_i(r)$ is usually tabulated at small r to more significant figures and at closer intervals than $P_i(r)$, it is much easier to differentiate accurately. Furthermore, at small r, $d\psi_i/dr$ is smaller than dP_i/dr, and the r^{2l+2} multiplicative factor reduces the integrand even more. The peak of the derivative is thus shifted out to large r and broadened. All these effects systematically help to improve the numerical accuracy of the results.

To illustrate these effects, we show in Fig. 1 a plot of the integrands in Eqs. (3) and (4) for the oxygen $1s$ Hartree-Fock function.[1] That this result is typical also for other representations is seen from the graphical study of the integrands in Eqs. (3) and (4) given in Fig. 2 for the $1s$ function $2a^{3/2}\exp(-ar)$ having $a=1$. For functions of higher quantum numbers, the simplifying effect of Eq. (4) is still more striking.

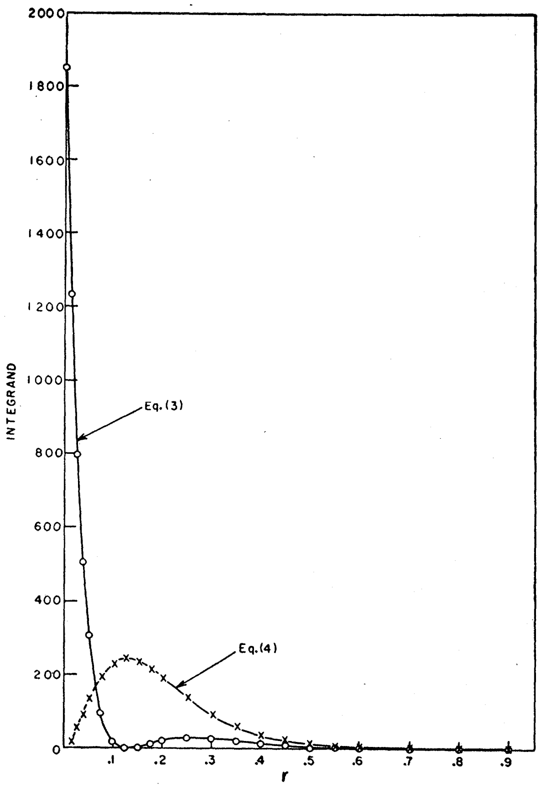

FIG. 1. Comparison between the integrands of Eqs. (3) and (4) for a typical Hartree-Fock $1s$ wave function. The crosses and circles indicate the r values at which the function is tabulated.

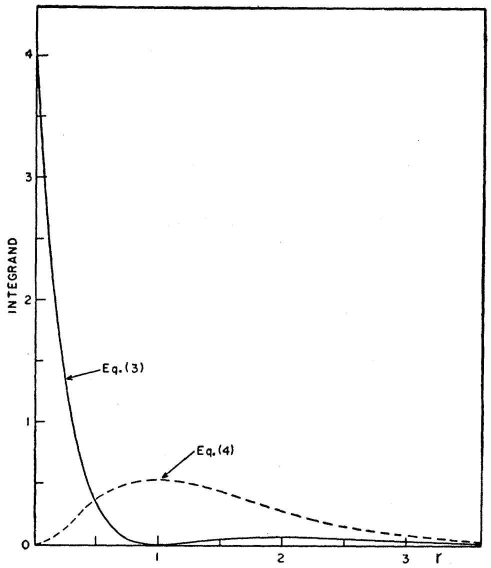

FIG. 2. Comparison between the integrands of Eqs. (3) and (4) for a typical $1s$ function $2a^{3/2}\exp(-ar)$ with $a=1$.

When the basis functions are of the simple Slater[2] form, or when the Hartree-Fock functions are expressed as linear combinations of such exponential functions,[3] Eq. (4) also results in another useful simplification. For example, for the simple $1s$ function cited above, the integrand in Eq. (3) is $(4r^2-8r+4)\exp(-2r)$ whereas the integrand of Eq. (4) is just $4r^2\exp(-2r)$. For more complicated wave functions the reduction of the algebraic computations is of course much greater.

The accuracy of this method has been tested in calculations on several atoms using Hartree-Fock functions. The kinetic energy integrals for atomic oxygen[4] and atomic nitrogen[5] were calculated by one of us (A.J.F.) using both Eqs. (3) and (4).[6] For oxygen and nitrogen the difference between the results obtained from Eqs. (3) and (4) was 0.066 and 0.064 Rydbergs, respectively, for the $1s$ electron and much smaller for the $2s$ and $2p$ electrons. Furthermore, the results of applying Eq. (4) gave a total kinetic energy which satisfied the virial theorem, whereas those of Eq. (3) did not.

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[6] As a test of accuracy, 5-point and 7-point differentiation formulas were used in separate calculations, and after doubling the integration intervals (at which the functions are tabulated), the calculations were repeated in order to determine the effect of the mesh size.