Use of Approximate Functions in Evaluating the Born Matrix Element for H_2^+ *

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The Born matrix element for the $1s\sigma_g$-$2p\sigma_u$ transition in H_2^+, at an internuclear separation R of $2.0a_0$, is calculated using the linear-combination-of-atomic-orbitals (LCAO) and screened LCAO functions for H_2^+. A comparison with the results found using the eigenfunctions and one other approximation is given. The R dependence of the error for these approximations is also investigated. The behavior of the Born matrix element for large momentum transfer is shown to be accurately predicted by these approximate functions for intermediate and large R. The small-momentum-transfer behavior is less accurately predicted. The usefulness of these approximate functions for extremes in the momentum transfer is correlated with their local behavior in space. The calculation of the total cross section for scattering of an electron and of a hydrogen atom with these approximate functions is discussed and compared with the results for the eigenfunctions.

APPROXIMATE electronic wave functions for the hydrogen molecule ion (H_2^+) are often employed because the complicated nature of the eigenfunctions for this system invites approximation. In this note we use H_2^+ as a model for testing approximate functions in evaluating the matrix element arising in the first Born approximation to scattering phenomena. For the case of inelastic scattering of electrons, this matrix element has been shown to be of the form[1]

$$|\epsilon(K,R)|^2=\left(\frac{1}{4\pi}\right)\int_0^{2\pi}\int_0^{\pi}\sin\delta d\delta d\xi \times\left|\int d\mathbf{r}\,\exp(i\mathbf{K}\cdot\mathbf{r})\Psi_n(\mathbf{r},R)\Psi_{n'}{}^*(\mathbf{r},R)\right|^2, \quad (1)$$

where Ψ_n and $\Psi_{n'}$ are the initial and final electronic eigenfunctions[2] of H_2^+, respectively. The angles δ, ξ orient $\mathbf{K}$ with respect to $\mathbf{R}$, where $\mathbf{K}$ is the momentum-transfer vector and $|\mathbf{R}|=R$ is the magnitude of the internuclear separation. Equation (1) has been evaluated with the H_2^+ eigenfunctions for a number of cases.[1] The result for the $1s\sigma_g$-$2p\sigma_u$ transition at $R=2.0a_0$ is shown in Fig. 1 as the solid curve labeled BLS (Bates, Ledsham, Stewart). This matrix element is here evaluated for the same case by replacing the eigenfunctions with

$$\Psi^{\pm}=N^{\pm}(\Phi_a{}^{\pm}\pm\Phi_b{}^{\pm}), \quad (2)$$

where $N^{\pm}$ is a normalization constant and

$$\Phi_i{}^{\pm}=[(z^{\pm})^3/\pi]^{1/2}\exp(-z^{\pm}r_i);$$

here r_i is the distance to the nucleus labeled i, and z^+, z^- are variational parameters appropriate to the σ_g, σ_u states, respectively. When $z^{\pm}=1$, Eq. (2) defines the linear combination of atomic orbitals (LCAO) functions for H_2^+, and the result for these functions is shown by the dotted curve in Fig. 1. For $R=2.0a_0$ the variational parameters z^+, z^- are 1.2387, 0.90045, respectively,[3] and the Born matrix element calculated with these functions is given by the dot-dash curve in Fig. 1. Finkelstein and Horowitz[4] (F-H) were the first to investigate the $1s\sigma_g$ case near $R=2.0a_0$ with a function of this form, hence these functions will be referred to as the F-H functions. The matrix element of Eq. (1) has also been evaluated by Ivash[5] where both screening parameters were taken equal to the F-H value, 1.228 for $R=2.01a_0$. This calculation has been repeated, taking $R=2.0a_0$, and is the solid curve labeled I in Fig. 1. A simple interpretation of the differences in these results can be given.

For very small K the integrand in Eq. (1) is strongly dependent on the behavior of the product $\Psi_n\Psi_{n'}{}^*$ at large distances from the nuclei,[6] that is, at large r. It is apparent that the LCAO and F-H functions are relatively poor in this respect. The functions used by Ivash give the best approximation in the small K range. However, taking $z^+=z^-\neq 1$ does not have any physical meaning and the value used must be considered a parameter introduced for the sake of convenience. It is, in fact, possible to find a value, $z^{\pm}=1.61$, that will make the Ivash calculation exact at $K=0$. However, from the arguments given below, it can be seen that this value will be quite poor for larger values of K.

At large K the Born matrix element will be most strongly dependent on the behavior of $\Psi_n\Psi_{n'}{}^*$ near the nuclei.[7] The values of $\Psi_n\Psi_{n'}{}^*$ at one of the nuclei are 0.207 for the eigenfunctions,[2] 0.193 for the LCAO functions,[2] 0.198 for the F-H functions, 0.098 for the functions used by Ivash, and 0.007 for $z^{\pm}=1.61$. The utility of the test of the functions at the nuclei is demonstrated by the good agreement at large K shown in Fig. 1 for

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[1] James M. Peek, Phys. Rev. 134, A877 (1964).

[2] D. R. Bates, Kathleen Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London A246, 215 (1953).

[3] James M. Peek, Sandia Corporation Report No. SC-RR-65-77 (unpublished).

[4] B. N. Finkelstein and G. E. Horowitz, Z. Physik 48, 118 (1928).

[5] E. V. Ivash, Phys. Rev. 112, 155 (1958).

[6] This is most easily seen by expanding $\exp(i\mathbf{K}\cdot\mathbf{r})$ in a power series and keeping the first nonvanishing term, which is $i\mathbf{K}\cdot\mathbf{r}$ for this dipole allowed transition.

[7] Because of the highly oscillatory nature of $\exp(i\mathbf{K}\cdot\mathbf{r})$ when $|\mathbf{K}|$ is large, contributions to the integral of Eq. (1) will be greatest from regions of rapidly changing $\Psi_n\Psi_{n'}{}^*$. In general, wave functions for systems of this type vary most rapidly near the nuclei.

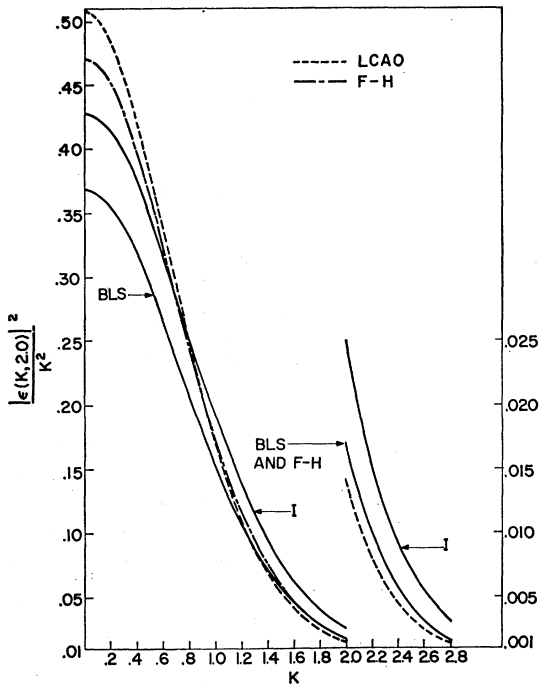

FIG. 1. $|\epsilon(K,2.0)|^2/K^2$ shown as a function of K, where both quantities are in atomic units. The curve labeled BLS was calculated with the H_2^+ eigenfunctions; I refers to the work of Ivash; the dotted curve is the LCAO results and the dot-dash curve is the F-H results. Note the scale change by a factor of 10 at $K=2.0$. For $K<2.0$ the ordinate is to the left and for $K>2.0$ the ordinate is to the right.

the LCAO and F-H functions, while the Ivash calculation is relatively inaccurate.

The dependence of these approximations to the Born matrix element on the internuclear separation is also of some interest since an integration over R is required to arrive at an observable quantity.[1] As $R\rightarrow 0$ the behavior of $\Psi_n\Psi_{n'}{}^*$ for the LCAO and F-H functions will be quite different. The F-H function for the $1s\sigma_g$ state goes to the correct eigenfunction in this limit where the LCAO function goes to a $1s$ hydrogenic orbital on a nucleus of charge one rather than two. Neither function has the correct limit for the $2p\sigma_u$ state[3] although the F-H function is expected to be somewhat better than the LCAO function because of the variational parameter. These functions are generally accepted to become better approximations as R is made large and, as shown in the next paragraph, this trend is observed for the Born matrix element.

The preceding discussion indicates that the behavior of $\Psi_n\Psi_{n'}{}^*$ near the nuclei for both functions becomes worse as R approaches zero; hence the large K dependence of the Born matrix element will not be accurately predicted by the LCAO and F-H functions. In fact, it is easily shown for $R=0$ that these functions predict $|\epsilon(K,0)|^2/K^2\sim K^{-8}$ for large K where the correct behavior is K^{-12}. The behavior of the LCAO functions near the nuclei has been shown to become more accurate as R increases.[2] This is borne out by numerical calculations at $R=3.2a_0$ where the LCAO functions are within 17% of the BLS results[2] and the F-H results differ by less than 10% in the range $1.0\leq K\leq 2.6$. The BLS case has not been studied for $R>3.2a_0$ but for large K and R the results for $R=3.2a_0$ indicate that fair accuracy can be obtained without the extensive labor required in using the eigenfunctions.

The small K behavior of the Born matrix element is most easily studied as a function of R by considering the dipole-length matrix element. We have the relationship

$$\lim_{K\rightarrow 0}|\epsilon(K,R)|^2K^{-2}=\tfrac{1}{3}|Q|^2, \tag{3}$$

where $|Q|$ is the dipole-length matrix element, hence $|Q|$ is a measure of the Born matrix element at the point $K=0$. $|Q|$ has been calculated by Bates[8] with the BLS and LCAO functions; these results are repeated in Fig. 2 by the curves labeled 1, 3, respectively. The F-H result is given by curve 4 and curve 2 is calculated with functions investigated by Cohen, Judd, and Riddell[9] (CJR). The formulas for $|Q|$ found for the F-H and CJR functions are available elsewhere[3] and will not be repeated here because of their length. The superiority of the F-H functions over the LCAO functions at small R is evident while for $R>2.0$ there is very little difference in the two approximations and, although the percentage error decreases, these approximate results differ from the correct values by roughly a constant for

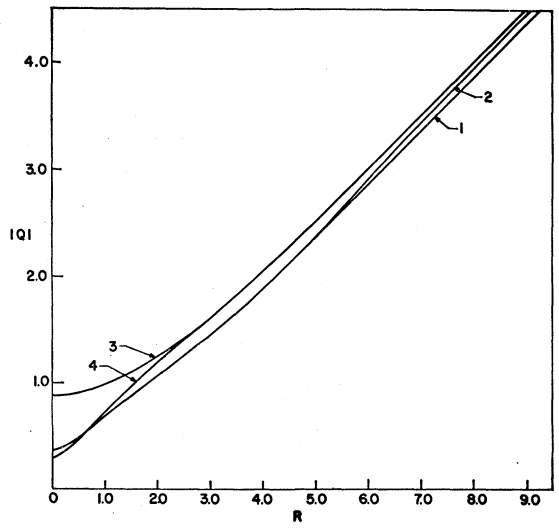

FIG. 2. The dipole-length matrix element shown as a function of R. Both quantities are in atomic units. Curve 1 was calculated with the eigenfunctions, curve 2 with the Cohen-Judd-Riddell functions (this curve is given only for $R\geq 1.5a_0$), curve 3 with the LCAO functions, and curve 4 with the Finkelstein-Horowitz functions.

[8] D. R. Bates, J. Chem. Phys. **19**, 1122 (1951).
[9] S. Cohen, D. Judd, and R. J. Riddell, Jr., University of California Radiation Laboratory Report No. UCRL-8802, 1959 (unpublished).

$4.0 \leq R \leq 9.0a_0$. It is also interesting that $|Q|$ for the CJR functions, which predict very accurate energies, departs from the BLS results (curve 1 in Fig. 2) and seems to be approaching the F-H, LCAO results at large R.

The argument based on the behavior of $\Psi_n\Psi_{n'}^*$ at large distances from the nuclei is difficult to apply for $3.0 \leq R \leq 9.0a_0$. This is because the region in space of interest is not clearly appropriate to either the combined atom or separated atom picture of H_2^+. In addition, it probably is the case that qualitative argument based on the local behavior of $\Psi_n\Psi_{n'}^*$ is not capable of explaining the (rather small) differences observed in this range of R or the unusually slow convergence to the BLS results as R becomes large.

When it is necessary to use approximate functions, the above arguments make it possible to pick the functions best suited to the situation.[10] As an example, consider the total cross section for two different types of processes calculated from the H_2^+ Born matrix elements shown in Fig. 1. The total cross section for the $1s\sigma_g$-$2p\sigma_u$ transition in H_2^+ caused by collision with an electron is proportional to the integral of the Born matrix element divided by K^3 and then integrated over momentum transfers allowed by energy conservation.[1] The information given in Fig. 1 shows that the cross section will then be dominated by small momentum transfers except for very low energy collisions. It has been shown for electron scattering[1] that the Ivash calculation gives errors of about 17% and calculation with the LCAO approximation gives twice this error. An analysis of $\Psi_n\Psi_{n'}^*$ at large distances from the nuclei, for these various functions, gives the same prediction, qualitatively, without extensive calculations.

The Born matrix element for the $1s\sigma_g$-$2p\sigma_u$ transition, when caused by a hydrogen atom, becomes

$$|\epsilon(K,R)|^2\{1-[16/(4+K^2)^2]\}^2, \qquad (4)$$

where $|\epsilon(K,R)|^2$ has the same significance as before. Dividing Eq. (4) by K^3 to obtain the integrand required to calculate the total cross sections for this case shows that the dominant momentum transfers are about 1 atomic unit. The LCAO results, for a hydrogen atom projectile, are about 7% higher than the BLS results and somewhat better than the Ivash approximation.

The R dependence of these two types of total cross sections is just what one expects from the discussion of R dependence given above. Calculations show for the internuclear separations of 1.4 and $3.2a_0$ that, in the electron case, the upper bounds to the errors found for the LCAO functions were 60 and 20%, respectively. The hydrogen atom case had upper bounds to the errors of 29 and 5%, respectively.

This example indicates that processes strongly dependent on large momentum transfers are rather accurately calculated by the LCAO functions, for intermediate or large R, and that these simple functions will serve quite well for most purposes. The prediction, by the LCAO functions, of processes dependent on small momentum transfers are found to have significant errors at intermediate values of R. To obtain high accuracy in this case, it is necessary to use more complicated wave functions, or as an alternative, empirically adjust the LCAO functions to give $\Psi_n\Psi_{n'}^*$ the correct behavior at large distances from the nuclei.

Note added in proof. A recent paper by D. R. Bates and A. R. Holt, in Proc. Phys. Soc. **85**, 691 (1965), provides an interesting treatment of a process dominated by small momentum transfer. In calculating the total cross section for the excitation of the $1s\sigma_g$-$2p\sigma_u$ transition in H_2^+ by a proton, they scale the LCAO Born matrix element by a ratio consisting of $|Q|^2$ calculated with the eigenfunctions[8] divided by the same matrix element evaluated with the LCAO functions. Hence Eq. (3) is satisfied in the sense that the scaled LCAO Born matrix element has the same small K limit as the Born matrix element evaluated with the eigenfunctions. This procedure, as can be demonstrated from the data given in Fig. 1, will lead to accurate total cross sections for this case if one restricts attention to relatively large collision energies. This restriction, already imposed by the first Born approximation, arises because of the dependence of the total cross section on large momentum transfers for small collision energies and the fact that this scaling is not valid for the larger momentum transfers.

The author wishes to express his gratitude to Thomas A. Green for many stimulating discussions on the use of approximate wave functions and to acknowledge the aid of Mrs. Marcella Madsen in performing the numerical analysis.

[10] The analysis given here is suggestive of a technique that utilizes a sectionally continuous potential. See, for an example, B. Zapol, P. Kunin, I. Taksar, and Z. Tsurule, Latvijas PSR Zinatnu Akad. Vestis No. 10 (195), 54–6 (1963). [Phys. Abstr. **67**, 2753 (1964).]