

# Basis set dependence of *ab initio* SCF elastic, Born, electron scattering cross sections for C<sub>2</sub>H<sub>4</sub>

Shang-de Xie<sup>a)</sup> and M. Fink

Department of Physics, The University of Texas at Austin, Austin, Texas 78712

D. A. Kohl

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

(Received 27 May 1983; accepted 23 March 1984)

The results of *ab initio* Hartree-Fock calculations of the orientationally averaged, elastic electron scattering cross section of C<sub>2</sub>H<sub>4</sub> with six different basis sets are reported. The averaging and Fourier transform were calculated by the approach of Kohl, Pulay, and Fink. Six different basis sets, ranging from 6-31G to 6-311 G<sup>4\*</sup>, were employed in the calculations. The improvement in the calculated Born cross section paralleled the lowering of the energy as the basis was varied. For C<sub>2</sub>H<sub>4</sub>, a calculation at the 6-311G<sup>\*\*</sup> level provides a good description of the cross section at a modest expenditure of computational time.

## I. INTRODUCTION

The success of the calculation of electron scattering cross sections in the first Born approximation from molecular wave functions suggested by Kohl, Pulay, and Fink<sup>1</sup> encouraged us to continue to compute other molecules. From the N<sub>2</sub> results<sup>2</sup> we know that it takes at least six *s*-type functions for the core electrons and three *s*- and *p*-type Gaussians for the valence electrons to represent the charge density around each nitrogen. The combination of these basis functions assured a proper asymptotic behavior at large scattering angles. The goal of this study was to test the sensitivity of the electron cross sections to additional terms in the basis set and to establish the optimum basis relative to the computer time and the expected data uncertainties ( $\pm 0.05\%$  of the cross section).

In order to assess the effect of the basis set on the calculation of the electron scattering cross section, we have performed the calculations for C<sub>2</sub>H<sub>4</sub> with six different basis sets. Each of the basis sets for the C atom start with an *s*-type inner-shell function with six Gaussians and an inner set of valence *s*- and *p*-type functions with three Gaussians. This set was expanded by 3,2,1 additional *s-p* functions and polarization functions. The basis sets used were 6-3111G<sup>4\*</sup>, 6-3111G, 6-311G<sup>\*\*</sup>, 6-311G, 6-31G, and 6-31G<sup>\*\*</sup>.

## II. BASIS SETS SELECTED

The largest set used here is the 6-311G<sup>\*</sup> basis<sup>3</sup> extended by the addition of one more outer *sp* Gaussian and one further *d* function for the carbon atoms. The hydrogen atom was enriched by the addition of one *sp* set with shared exponent and one more *p* function. The exponents of the polarization and diffuse functions are given in the Appendix for all basis sets. Besides 6-3111G<sup>4\*</sup>, 6-3111G, 6-311G<sup>\*\*</sup>, and 6-311G, we did the same calculation with 6-31G<sup>\*\*4</sup> and 6-31G<sup>5</sup> basis sets for comparison. The calculated molecular energies and the time required for the calculation of the SCF wave function and the scattering intensities with these different basis sets are listed in the Appendix. The energies calcu-

lated from the 6-3111G<sup>4\*</sup> or 6-311G<sup>\*\*</sup> basis sets are significantly lower than the energies from the other four. We now need to examine the sensitivity of the scattering cross section to these six basis sets.

## III. SCATTERING EVALUATION METHOD

The Born scattering amplitude is the Fourier transform of the molecular electron density

$$F(s) = \int \rho(\mathbf{r}) \exp(\mathbf{s} \cdot \mathbf{r}) d\mathbf{r} = \sum_{\mu\nu} \int \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \exp(\mathbf{s} \cdot \mathbf{r}) d\mathbf{r}. \quad (1)$$

Here  $\mathbf{s}$  is the momentum transfer vector  $[(4\pi/\lambda) \sin \frac{1}{2}\theta]$ ,  $\rho(\mathbf{r})$  is the electron nuclear density and  $\chi_{\mu}, \chi_{\nu}$  are basis functions, in our case Gaussians.

The spherically averaged differential cross section multiplied by the fourth power of the absolute value of the momentum transfer  $s$  is given by

$$I(s) = s^4 \left( \frac{d\sigma}{d\Omega} \right) = \pi^{-1} \int \left| \sum_a Z_a \exp(\mathbf{s} \cdot \mathbf{R}_a) - F(s) \right|^2 d\Omega_s, \quad (2)$$

where  $Z_a$  and  $\mathbf{R}_a$  are the charge and position vector of nucleus  $a$  and  $\Omega_s$  denotes the solid angle.  $\Omega_s$  stands for all possible orientations between the incoming electron and the molecular axes.

The independent atom model IAM is a good approximation to the cross section. This model is based on the construction of molecular scattering amplitudes  $F_{\text{IAM}}(\mathbf{s})$  from a superposition of spherical atomic scattering amplitudes. For later comparisons, we define  $\Delta I$ :

$$\Delta I = I - I_{\text{IAM}} \quad (3)$$

where  $I_{\text{IAM}}$  is obtained by substituting  $F_{\text{IAM}}(\mathbf{s})$  for  $F(\mathbf{s})$  in Eq. (2).

Analytical spherical averaging requires the calculation of two kinds of integrals, obtained by expanding the square in Eq. (2). The electron-nucleus interference integrals are

$$\iint d\Omega \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \exp[is \cdot (\mathbf{r} - \mathbf{R}_a)] d\mathbf{r}. \quad (4)$$

Here  $\mathbf{R}_a$  is the position vector of the nucleus  $a$ , and  $\mu, \nu$  are

<sup>a)</sup> Permanent address: Department of Physics, Shanxi University, Taiyuan, Shanxi, China.

indices of the basis functions. This integral, including the orientational ( $\Omega$ ) average, is evaluated analytically.<sup>1</sup> The evaluation of the electron–electron interference terms, however, presents difficulties. We give here a brief recapitulation of our method; a full account is given in Ref. 1. In order to evaluate analytically the spherical average of the electron–electron interference

$$\int |F(\mathbf{s})|^2 d\Omega, \quad (5)$$

one has to evaluate elementary integrals of the form

$$\iiint d\Omega \chi_\mu(\mathbf{r}_1) \chi_\nu(\mathbf{r}_1) \chi_\rho(\mathbf{r}_2) \chi_\sigma(\mathbf{r}_2) \exp[\mathbf{s} \cdot (\mathbf{r}_1 - \mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2. \quad (6)$$

These integrals, due to the spherical averaging, are nonseparable in the electronic coordinates  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . We have thus to deal with  $O(N^4)$  integrals, instead of  $O(N^2)$  amplitudes  $F(\mathbf{s})$ . This difficulty is eliminated when the amplitudes are first calculated analytically and then added and squared. The subsequent orientational averaging of expression (6) must be executed numerically; unfortunately this procedure becomes unstable for high  $|\mathbf{s}|$  values, due to the oscillatory nature of the integrand. Our new technique makes use of the fact that the amplitudes  $F(\mathbf{s})$  are very well approximated by the IAM model, particularly at high  $|\mathbf{s}|$  values. We define the difference amplitude

$$F'(s) = F(s) - F_{\text{IAM}}(s) \quad (7)$$

and expand Eq. (5) as

$$\int d\Omega |F_{\text{IAM}}(s)|^2 + 2 \operatorname{Re} \int d\Omega F_{\text{IAM}}^*(s) F'(s) + \int d\Omega |F'(s)|^2. \quad (8)$$

In this equation, the first term is trivial, and the second is of the same form as Eq. (4), and is evaluated by an accurate analytical formula. Only the last term must be evaluated numerically. This term is the square of a quantity already small and practically vanishes above  $|s| = 10 \text{ \AA}^{-1}$ , where the numerical integration becomes difficult.<sup>1</sup> We believe that this combination of analytical and numerical integration techniques is the most efficient way to calculate elastic Born scattering cross sections. The last term in Eq. (8) is somewhat loosely referred to as the contribution of the electron–electron interference term to the scattering intensity in Ref. 2 (the quantity  $I''$  in Table III of Ref. 2).

Ethylene has  $D_{2h}$  symmetry. In the calculation full advantage is taken of this group, both in the SCF calculation and in the orientational averaging. Considering the symmetry of C<sub>2</sub>H<sub>4</sub> molecule,  $\theta$  and  $\Phi$  are varied only from  $0^\circ$  to  $90^\circ$ .

TABLE I. Total molecular energies and TM time consumed for the various basis sets used. Also maximum deviation in the intensities relative to the 6-3111G<sup>4\*</sup> are listed.

	6-3111G <sup>4*</sup>	6-311G <sup>**</sup>	6-3111G	6-311G	6-31G <sup>**</sup>	6-31G
$E$ (hartrees) <sup>a</sup>	-78.060 73	-78.054 49	-78.020 65	-78.019 28	-78.034 70	-77.997 82
$T_1(s)$ <sup>b</sup>	2161	548	220	197	293	101
$T_2(s)$ <sup>c</sup>	2960	1642	1299	980	1514	708
$T_1 + T_2$ <sup>b,c</sup>	5120	2190	1519	1177	1807	809
$\Delta I - \Delta I_0$ <sup>d</sup>	0	0.037	0.282	0.295	0.204	0.260

<sup>a</sup>  $E$  = calculated molecular energy.

<sup>b</sup>  $T_1$  = TM time for integrals in the SCF calculation.

<sup>c</sup>  $T_2$  = TM time for scattering integrals and intensities.

<sup>d</sup>  $\Delta I - \Delta I_0$  = the difference of the largest extreme of the calculated results relative to the 6-3111G<sup>4\*</sup> basis set.

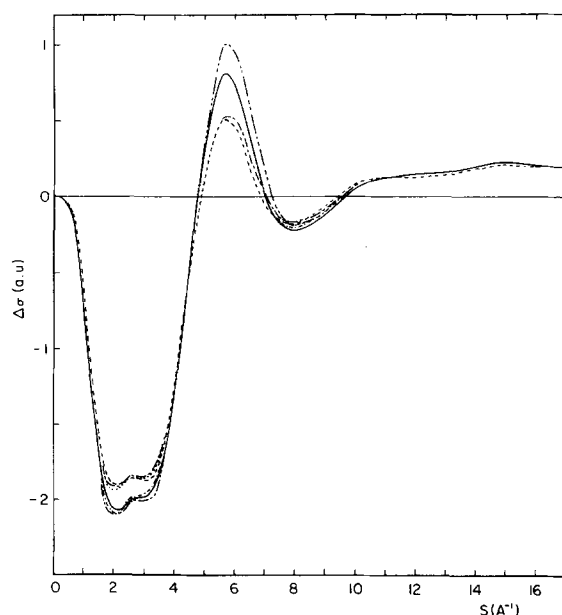


FIG. 1. Difference between electron scattering cross sections based on molecular wave functions and the atomic independent model for C<sub>2</sub>H<sub>4</sub>. - (6-3111G<sup>4\*</sup>); -- (6-311G<sup>\*\*</sup>); --- (6-31G<sup>\*\*</sup>); - - (6-311G); ... (6-311G); --- (6-311G).

This octant is represented by 40 pairs of  $\theta$  and  $\Phi$ . For each pair ( $\theta, \Phi$ ), the scattering amplitude is evaluated and the sum of all pairs represents the orientational averaged cross section  $I$  for each  $s$  value.

#### IV. EVALUATION OF THE BASIS SET TESTS

Figure 1 shows our calculated  $\Delta I$  values of C<sub>2</sub>H<sub>4</sub> for the different basis sets. The molecular geometry is fixed to  $r(\text{CC}) = 1.330 \text{ \AA}$ ,  $r(\text{CH}) = 1.076 \text{ \AA}$ , and  $\angle(\text{HCH}) = 116.6^\circ$ . At higher  $s$  values ( $s > 10 \text{ \AA}^{-1}$ ), the difference between the different basis sets is very small. This confirms the expectation that the polarization functions are not important at large  $s$  values. The first nodal point is almost the same (near  $s = 4.8 \text{ \AA}^{-1}$ ) for all basis sets. The 6-3111G<sup>4\*</sup> and 6-311G<sup>\*\*</sup> curves nearly coincide. The maximum of  $|\Delta I_{6-311G^{**}} - \Delta I_{6-3111G^{4*}}|$  is 0.037 a.u., which is about 0.1% of  $I$ . The 6-3111G, 6-311G, and 6-31G curves are very similar. Though the basis sets have a different number of  $sp$  functions, they do not include  $d$  (for C) and  $p$  (for H) polarization functions. The total energies between these three functions change up to 0.02 a.u. (see Table I). Nevertheless no appreciable convergence toward the H–F limit is visible. This demonstrates very instructively how the cross sections are

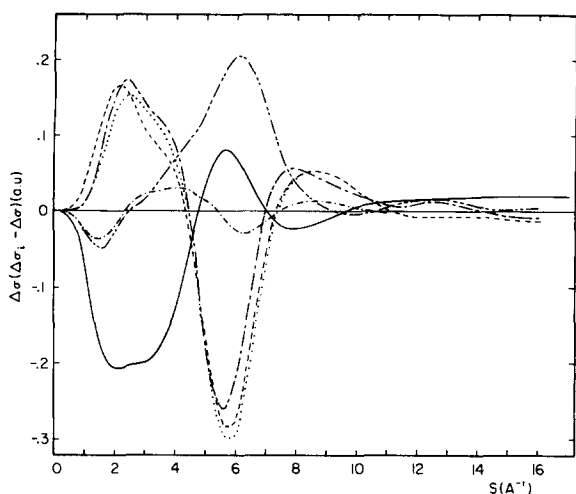


FIG. 2. Difference between electron scattering cross section based on various molecular wave functions and the result based on the 6-3111G\*\* basis set. Identification of lines (see Fig. 1).

sensitive to the additional flexibility of the  $d$  functions in the basis set. This phenomena can be seen particularly well when the  $\Delta I$  curves as shown in Fig. 2 are studied. The reference function was chosen to be the  $\Delta I$  (6-3111G\*\*) result.

The cross section difference series derived from the 6-31G, 6-311G, and 6-3111G basis sets shows that an overall description of the density is not improved by adding more valence functions of the same symmetry to an optimized basis set (here the 6-31G). It may smooth out the electron distribution function leading to a slight lowering of the energy. The differential cross sections also show no particular sensitivity to this type of change in the basis. The expansion of the basis set to  $d$  (and  $p$ ) functions however makes a significant change. Unfortunately, the additions often interfere with the former optimization and the resulting cross section will change but in a rather uncontrolled fashion. This behavior is documented in the comparison of the 6-31G and 6-31G\*\* results. With the 6-311G\*\* we deal again with an optimized set and the cross section comes to within the error limits to the 6-3111G\*\* results. However, it should be noted that the quadruple zeta set is in itself a spinoff from the 6-311G\*\* and the close agreement is not quite unexpected. Our results parallel the findings by Hase and Schweig.<sup>6</sup> They studied the effect of the basis sets on NCCN with regard to the charge density difference maps. After polarization functions had been introduced into the basis set no further improvement was found by extending the number of basis functions.

The  $\Delta I$  curves have two contributions. One originates from the electron-nuclear interference term in the first Born expression (2ZF) and the second describes the electron-electron scattering ( $F^2$ ). Analogously, there is a  $\Delta I_{ne}$  and a  $\Delta I_{ee}$  contribution to  $\Delta I$ . As seen in Eq. (8)  $\Delta I_{ee}$  has two contributions, one of which is evaluated analytically and  $d\Omega |F'(s)|^2$  is calculated numerically. As already found for N<sub>2</sub>, the latter term is very small and in Fig. 2 contributes less than 5% to the extreme of the plotted  $\Delta I$  functions.

## V. CONCLUSIONS

The calculations of the cross sections from various molecular SCF wave functions showed that there is a measur-

able difference between the results, depending on which basis set is used. We found that polarization functions and an optimized set are necessary to guarantee the required accuracy in the description of the charge density and consequently the cross sections. While the lowest energy of C<sub>2</sub>H<sub>4</sub> lies below the best previous SCF results,<sup>7</sup> we still lack about 0.29 hartrees of correlation energy. To what extent this correlation energy will become visible in the elastic differential cross sections has to be guessed at present. Previous experience gives reason to be hopeful that the SCF calculation on the level of our 6-311G\*\* basis might be sufficient. In the case of atoms this comparison between CI and SCF has been made for Ne and very little change was found in the elastic cross section<sup>8</sup> (in strong contrast to the inelastic channels). Similar agreement was found for NH<sub>3</sub> where the calculations of Ostlund *et al.*<sup>9</sup> agreed extremely well with the elastic electron scattering data of Duguet.<sup>10</sup> At present it appears to be justifiable to use SCF cross sections of the 6-311G\*\* level to correct electron diffraction data to remove the oscillatory background, which can interfere with routine structure determination. Experiments presently underway in one of our laboratories will lead to elastic cross sections which can be compared with these calculations directly.

## ACKNOWLEDGMENTS

This work was supported in part by the Robert A. Welch Foundation and by the National Science Foundation Grant CHE 8007940. The authors thank Dr. Pulay for many valuable suggestions and a critical review of this manuscript.

## APPENDIX: GAUSSIAN BASIS SETS FOR C<sub>2</sub>H<sub>4</sub>

6-3111G\*\* is a 6-113G\*\* basis set<sup>3</sup> augmented by two sets of uncontracted  $d$  functions ( $\exp = 1.0843$  and  $0.3574$ ) and a set of diffuse  $sp$  functions ( $\exp = 0.05$ ) on C; two  $p$  type functions ( $\exp = 1.299$  and  $0.433$ ) and a diffuse  $s$  function ( $\exp = 0.03$ ) on H.

6-3111G is the same as 6-3111G\*\* excluding the  $d$  functions on C and the  $p$  functions on H.

6-311G\*\* is the basis set given in Ref. 3.

6-311G is the same as 6-311G\*\* omitting the  $d$  function on C and the  $p$  function on H.

6-31G\*\* is the basis set given in Ref. 4.

6-31G is the basis set given in Ref. 5.

<sup>1</sup>D. A. Kohl, P. Pulay, and M. Fink, *Theochem.* **17**, 149 (1984).

<sup>2</sup>P. Pulay, R. Mawhorter, D. A. Kohl, and M. Fink, *J. Chem. Phys.* **79**, 185 (1983).

<sup>3</sup>R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).

<sup>4</sup>P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta. (Berlin)* **28**, 213 (1973).

<sup>5</sup>W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).

<sup>6</sup>H. L. Hase and A. Schweig, *Angew. Chem.* **89**, 264 (1977).

<sup>7</sup>P. Saxe, D. J. Fox, H. F. Schaefer III, and N. C. Handy, *J. Chem. Phys.* **77**, 5584 (1982).

<sup>8</sup>R. A. Bonham and M. Fink, *High Energy Electron Diffraction* (Van Nostrand-Reinhold, New York, 1974).

<sup>9</sup>A. Szabo and N. Ostlund (their results are listed in Ref. 10 as a private communication).

<sup>10</sup>A. Duguet, "Diffusion Elastique et Inelastique d'Electrons Rapides par la Molecule NH<sub>3</sub> et les Atomes Ne et Ar," Ph.D. thesis, University de Paris-Sud, 1981.