

### Small-angle elastic electron scattering and moments of the molecular electronic charge density

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The first-Born-approximation expression for elastic scattering by molecules in the gas phase is expanded in a power series in the momentum transfer. It is shown that this expansion can be fitted to high-energy electron scattering measurements to obtain accurate estimates of the mean-square radius of molecules. In addition, by use of information on the molecular quadrupole moment and the molecular structure, the electronic moments  $\langle x^2 \rangle$  and  $\langle z^2 \rangle$ , and the diamagnetic susceptibility may be calculated. It also appears possible to obtain information on some of the higher electronic moments such as  $\langle r^4 \rangle$ . Results are given for H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>.

It is well known that the small-angle elastic electron scattering in the high-energy limit can be expanded in a power series in the momentum transfer.<sup>1</sup> It does not appear, however, that serious attempts to fit such expansions to actual scattering data for molecules with the aim of extracting information on the moments of the molecular

electronic charge density have been attempted. It is the purpose of this work to explore this possibility.

In the first Born approximation<sup>2</sup> the elastic electron scattering from a free molecule averaged over the rotational motion can be written as

$$\left( \frac{d\sigma}{d\Omega} \right)_{el} = \frac{4\gamma^2}{a_0^2 K^2} \left[ \sum_{n=1}^M \sum_{m=1}^M Z_n Z_m j_0(KR_{nm}) - 2 \sum_{n=1}^M Z_n \int d\mathbf{r} \rho(\mathbf{r}) j_0(K|\mathbf{R}_n - \mathbf{r}|) + \int d\mathbf{r} \rho(\mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') j_0(K|\mathbf{r} - \mathbf{r}'|) \right], \tag{1}$$

where  $(d\sigma/d\Omega)_{el}$  is the elastic differential cross section,  $K$  is the momentum transfer,  $a_0$  is the Bohr radius,  $\gamma^2$  is  $1/(1-\beta^2)$  with  $\beta=v/c$ ,  $v$  is the velocity of the electron, and  $c$  is the velocity of light. The quantity  $Z_n$  is the atomic number of the  $n$ th of  $M$  nuclei located at the point  $\mathbf{R}_n$ ,  $\rho(\mathbf{r})$  is the electron charge density of the molecule at the point  $\mathbf{r}$ ,  $j_0(x)$  is a spherical Bessel function ( $\sin x/x$ ), and the origin is chosen as the center of mass of the molecule with a principle axis coordinate system<sup>3</sup> where the  $z$  axis is parallel to the axis of greatest molecular symmetry.

The spherical Bessel functions may all be expanded as<sup>4</sup>

$$j_0(K|\mathbf{a} - \mathbf{b}|) = \sum_{n=0}^{\infty} (2n+1)2^{2n} \sum_{m=-n}^n C_{nm}(\theta_a, \varphi_a) C_{nm}^*(\theta_b, \varphi_b) \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \frac{(-1)^{k+l} (n+k)! (n+l)! a^{n+2k} b^{n+2l} K^{2k+2l+2n}}{k! l! (2n+2k+1)! (2n+2l+1)!} \tag{2}$$

which can be used to rewrite Eq. (1) in terms of quantities related to spherical tensors,<sup>5</sup> in Hartree atomic units, as

$$\begin{aligned} \left[ \left( \frac{d\sigma}{d\Omega} \right)_{el} / (\gamma^2 a_0^2) \right] &= \frac{4}{3K^2} |Q_{1m}^1|^2 + \frac{1}{9} (|Q_{00}^2|^2 + \frac{4}{5} |Q_{2m}^2|^2 - \frac{12}{5} \text{Re} Q_{1m}^{3*} Q_{1m}^1) \\ &- \frac{K^2}{90} (\text{Re} Q_{00}^{4*} Q_{00}^2 - \frac{6}{5} |Q_{1m}^3|^2 - \frac{6}{7} \text{Re} Q_{1m}^{5*} Q_{1m}^1 + \frac{8}{7} \text{Re} Q_{2m}^{4*} Q_{2m}^2 - \frac{8}{35} |Q_{3m}^3|^2) \\ &+ \frac{K^4}{3600} [ |Q_{00}^4|^2 + \frac{20}{21} \text{Re} Q_{00}^{6*} Q_{00}^2 - \frac{24}{7} \text{Re} Q_{1m}^{5*} Q_{1m}^3 - \frac{40}{63} \text{Re} Q_{1m}^{7*} Q_{1m}^1 + \frac{80}{49} |Q_{2m}^4|^2 + \frac{80}{63} \text{Re} Q_{2m}^{6*} Q_{2m}^2 \\ &- \frac{64}{63} \text{Re} Q_{3m}^{5*} Q_{3m}^3 + \frac{64}{441} |Q_{4m}^4|^2 ] + O(K^6), \tag{3} \end{aligned}$$

where  $\text{Re}$  signifies the real part,  $m$  is summed over all allowed values, and

$$Q_{Lm}^l = \sum_{n=1}^M Z_n R_n^l C_{Lm}(\theta_n, \varphi_n) - \int d\mathbf{r} \rho(\mathbf{r}) r^l C_{Lm}(\theta_r, \varphi_r). \tag{4}$$

The  $C_{Lm}$  times  $(\sqrt{2L+1}/\sqrt{4\pi})$  are the normalized spherical Harmonics,<sup>5</sup>  $Y_{Lm}$ . Equation (3) is understood to be averaged over the vibrational motion of the molecule. In order to connect the spherical tensors  $Q_{Lm}^i$  with the usually used Cartesian tensors the expansion<sup>4</sup>

$$R^i C_{Lm}^{(i \geq L)} = \frac{(-1)^m}{2^L} \left[ \frac{(L-|m|)!}{(L+|m|)!} \right]^{1/2} \sum_{k=0}^{|m|} \sum_{j=0}^M \frac{i^k (-1)^j (2L-2j)! |m|! X^{|m|-k} Y^k Z^{L-2j-|m|} R^{l+2j-L}}{j! k! (L-j)! (L-2j-|m|)! (|m|-k)!}, \quad (5)$$

with  $M$  the largest integer  $\leq [(L-|m|)/2]$ , can be employed with the usual definition of the electric moments<sup>6</sup>

$$M_{\alpha\beta\gamma\delta \dots} = (-1)^\nu \left\langle \frac{R^{(2\nu+1)}}{\nu!} \frac{\partial^\nu}{\partial R_\alpha \partial R_\beta \partial R_\gamma \partial R_\delta \dots} \left[ \frac{1}{R} \right] \right\rangle, \quad (6)$$

where  $\nu$  is the total number of differentiations and the angular brackets,  $\langle \rangle$ , signify all appropriate averages.

By use of molecular symmetry Eq. (3) can usually be simplified.<sup>4</sup> For a linear molecule with a permanent dipole moment one has<sup>7</sup>

$$\begin{aligned} \left[ \frac{d\sigma}{d\Omega} \right]_{\text{el}} / (\gamma^2 a_0^2) &= \frac{4}{3K^2} \mu^2 + \frac{1}{9} \langle R^2 \rangle^2 + \frac{4}{5} Q^2 - \frac{12}{5} \langle R^2 \mu \rangle \mu \\ &- \frac{K^2}{90} (\langle R^4 \rangle \langle R^2 \rangle - \frac{6}{5} \langle R^2 \mu \rangle^2 - \frac{6}{7} \langle R^4 \mu \rangle \mu + \frac{8}{7} \langle R^2 Q \rangle Q - \frac{8}{35} \Omega^2) \\ &+ \frac{K^4}{3600} (\langle R^4 \rangle^2 + \frac{20}{21} \langle R^6 \rangle \langle R^2 \rangle - \frac{24}{7} \langle R^4 \mu \rangle \langle R^2 \mu \rangle - \frac{40}{63} \langle R^6 \mu \rangle \mu + \frac{80}{49} \langle R^2 Q \rangle^2 + \frac{80}{63} \langle R^4 Q \rangle Q \\ &- \frac{64}{63} \langle R^2 \Omega \rangle \Omega + \frac{64}{441} \Phi^2) + O(K^6), \end{aligned} \quad (7)$$

where  $\mu$ ,  $Q$ ,  $\Omega$ , and  $\Phi$  are the total dipole, quadrupole, octopole, and hexadecapole moments, respectively.<sup>7</sup> The notation  $R^2\Omega$ , for example, is the average of the product  $R^2\Omega_{ZZZ}$  where capital letters signify that all quantities are the differences between nuclear and electronic contributions written in this case as  $\sum_n Z_n R_n^5 \cos^3 \theta_n - \langle r^2 z^3 \rangle$ . For a linear molecule with no dipole moment both  $\mu$  and  $\Omega$  vanish and one has

$$\begin{aligned} \left[ \frac{d\sigma}{d\Omega} \right]_{\text{el}} / (\gamma^2 a_0^2) &= \frac{1}{9} \langle R^2 \rangle^2 + \frac{4}{5} Q^2 - \frac{K^2}{90} (\langle R^4 \rangle \langle R^2 \rangle + \frac{8}{7} \langle R^2 Q \rangle Q) + \frac{K^4}{3600} (\langle R^4 \rangle^2 + \frac{20}{21} \langle R^6 \rangle \langle R^2 \rangle + \frac{80}{49} \langle R^2 Q \rangle^2 \\ &+ \frac{80}{63} \langle R^4 Q \rangle Q + \frac{64}{441} \Phi^2) + O(K^6). \end{aligned} \quad (8)$$

For tetrahedral molecules both  $\mu$  and  $Q$  vanish and one has<sup>8</sup>

$$\begin{aligned} \left[ \frac{d\sigma}{d\Omega} \right]_{\text{el}} / (\gamma^2 a_0^2) &= \frac{1}{9} \langle R^2 \rangle^2 - \frac{K^2}{90} (\langle R^4 \rangle \langle R^2 \rangle - \frac{96}{175} \Omega^2) + \frac{K^4}{3600} (\langle R^4 \rangle^2 + \frac{20}{21} \langle R^6 \rangle \langle R^2 \rangle \\ &- \frac{256}{105} \langle R^2 \Omega \rangle \Omega + \frac{256}{1029} \Phi^2) + O(K^6), \end{aligned} \quad (9)$$

where

$$\Omega = \frac{5}{2} \langle XYZ \rangle = \sum_n Z_n R_n^3 \cos \theta_n \sin^2 \theta_n \cos \varphi_n \sin \varphi_n - \langle xyz \rangle.$$

The octahedral case is simpler still since all moments through the octopole moment vanish and the result is

$$\begin{aligned} \left[ \frac{d\sigma}{d\Omega} \right]_{\text{el}} / (\gamma^2 a_0^2) &= \frac{1}{9} \langle R^2 \rangle^2 - \frac{K^2}{90} \langle R^4 \rangle \langle R^2 \rangle \\ &+ \frac{K^4}{3600} (\langle R^4 \rangle^2 + \frac{20}{21} \langle R^6 \rangle \langle R^2 \rangle \\ &+ \frac{256}{1029} \Phi^2), \end{aligned} \quad (10)$$

In order to apply Eqs. (6)–(10) to actual experimental

scattering data a number of corrections are necessary to reduce the data to the first Born level. The most obvious correction is division of the data by  $\gamma^2$  to take care of relativistic effects on the scattered electron. This correction is justified from comparisons of nonrelativistic Born scattering amplitudes multiplied by  $\gamma^2$  with relativistic partial wave scattering amplitudes for atomic hydrogen where partial wave effects are unimportant.<sup>9</sup> The second correction, which becomes increasingly important for heavier systems or lower incident electron energies, is intramolecular multiple scattering. This is just the difference between the Born approximation result and the exact treatment of the scattering problem for a static nonspherical molecular potential. Because of the difficulty in obtaining the exact solution to the static problem the in-

dependent atom model<sup>2</sup> (IAM) using partial wave (PW) atomic scattering factors<sup>9</sup> is used to estimate this correction. This omits multiple scattering between different atoms in the molecule, but Kohl and Arvedson<sup>10</sup> have shown that in light systems, such as  $N_2$ , that the effect is small for energies above 20 keV. This effect *reduces* the cross section in the forward direction.

A third effect comes from distortion of the molecular electron distribution by the presence of the scattering electron. This is often referred to as a polarization and/or absorption effect and generally *increases* the cross section in the forward direction. Polarization and absorption increase with increasing target polarizability and decreasing electron beam energy. We have used second Born results for H and He to obtain an empirical polarization amplitude of the form<sup>11</sup>

$$f^{\text{pol}}(K) = \frac{\beta_0}{E^{1/2}} e^{-K\gamma_0 E^{1/2}},$$

where  $E$  is the incident electron energy,  $\beta_0 = \pi\alpha |E_T|^{1/2}/4N^\nu$ , and  $\gamma_0 = N^\nu/|E_T|^{1/2}$  with  $\alpha$  the static polarizability,  $|E_T|$  the absolute value of the total target electronic energy, and  $N$  the total number of electrons in the target. The parameter  $\nu$  was chosen to fit the second Born results for H and He over the energy range 500–50 000 eV (Ref. 11) and the experimental and theoretical results for Ne at 500 eV.<sup>12</sup> In order to obtain some estimate for this effect, we have assumed that this simple formula can be applied to molecules as well. This can serve as an upper bound for how large the effect can be since the corrected intensity values as  $K \rightarrow 0$  must not have a positive slope with increasing momentum transfer. Any correction which causes the corrected intensity to decrease as  $K \rightarrow 0$  must therefore be regarded as unrealistically large. At high incident electron energies polarization will be largely confined to very small angles. Fits of the type envisioned here are incapable of reproducing the exponential shape of the polarization correction in the region not observed by the experiment and hence the asymptotic value at  $K=0$  will only be influenced by the

size of the corrections in the region where data are available.

The final correction is for electron exchange in the scattering process. The exchange amplitude for elastic scattering in the high-energy Born approximation assumes the form<sup>13</sup>  $\gamma F(K)/(2a_0E)$  where  $F(K)$  is the molecular x-ray coherent scattering factor and  $E$  is the incident electron energy in Hartree's. In the small angle range the exchange amplitude is close to  $\gamma N/(2a_0E)$  where  $N$  is the total number of electrons in the molecule and leads to an *increase* in the forward cross section. This correction is generally less than 1% for incident electron energies greater than 20 keV. In Table I we give a listing of the estimated corrections for the zero angle asymptotes of the experimental cross sections considered in this study. The final corrected values are of course vibrationally averaged quantities.

In order to compare the results of this study with those obtained from theory or from other types of experiments such as magnetic susceptibility and electric moment measurements, the problem of vibrational averaging must be considered. The basic quantities extracted from the electron scattering experiment are of the form  $\langle\langle R^2 \rangle\rangle_{\text{vib}}$  which indicates the vibrational average of the square of another type of average such as an electronic average. Experiments which yield data that can be used to calculate a scattering cross section typically yield  $\langle\langle R^2 \rangle\rangle_{\text{vib}}$  or the vibrational average of the same quantity without being squared. It is therefore of interest to consider the difference  $\langle\langle R^2 \rangle\rangle_{\text{vib}} - \langle\langle R^2 \rangle\rangle_{\text{vib}}^2$ . If both  $\langle R^2 \rangle^2$  and  $\langle R^2 \rangle$  are expanded in normal coordinates then the difference between the two ways of averaging to lowest order can be written as

$$\langle\langle R^2 \rangle\rangle_{\text{vib}} - \langle\langle R^2 \rangle\rangle_{\text{vib}}^2 = \sum_i \sum_j \frac{\partial \langle R^2 \rangle}{\partial q_i} \frac{\partial \langle R^2 \rangle}{\partial q_j} \times (\langle q_i q_j \rangle - \langle q_i \rangle \langle q_j \rangle), \quad (11)$$

TABLE I. Experimental estimates of the elastic cross section at zero scattering angle,  $[d\sigma(0)/d\Omega]_{\text{el}}/\gamma^2 a_0^2$  and corrections for partial wave, polarization, and exchange effects.

Molecule	Energy (keV)	Cross section (a.u.)	Partial wave correction (a.u.)	Polarization <sup>d</sup> correction (a.u.)	Exchange correction (a.u.)	Corrected cross section (a.u.)
H <sub>2</sub>	25	2.0±0.2 <sup>a</sup>	0.0	0.0	-0.003	2.0±0.2
N <sub>2</sub>	37	47±3 <sup>b</sup>	0.5	-0.8	-0.07	47±3
	30	53±1.5 <sup>c</sup>	0.7	-1.2	-0.09	54±1.5
O <sub>2</sub>	60	45±3 <sup>b</sup>	0.6	-0.4	-0.05	46±3
	37	43±3 <sup>b</sup>	0.8	-1.0	-0.08	44±3

<sup>a</sup>Reference 14.

<sup>b</sup>Reference 15.

<sup>c</sup>Reference 16.

<sup>d</sup>This is an estimate of the maximum possible effect. This correction was not applied since its application to experimental values led to a slight positive slope of the corrected cross section in the range  $0.2 < K \text{ (a.u.)} < 0.3$ .

TABLE II. Parameters used to calculate the difference due to vibrational averaging between the zero-angle Born elastic cross section and that calculated from magnetic susceptibility data.

Molecule	Bond length (a.u.)	$\langle q \rangle$ (a.u.) $T=300$ K	$\langle q^2 \rangle$ (a.u.) $T=300$ K	$\frac{\partial \langle r^2 \rangle}{\partial q}$ (a.u.)	$\frac{\partial Q_{\text{tot}}}{\partial q}$	$\Delta \left[ \frac{d\sigma(0)}{d\Omega} \right]_{\text{el}}^c$
H <sub>2</sub>	1.402 <sup>a</sup>	0.042 <sup>a</sup>	0.0305 <sup>a</sup>	+ 2.6 <sup>b</sup>	+ 1.3 <sup>b</sup>	+ 0.009
N <sub>2</sub>	2.0742 <sup>a</sup>	0.0083 <sup>a</sup>	0.0038 <sup>a</sup>	+ 17 <sup>c</sup>	+ 1.3 <sup>c,d</sup>	+ 0.003

<sup>a</sup>See Ref. 17.

<sup>b</sup>See Ref. 18.

<sup>c</sup>See Ref. 19.

<sup>d</sup>See Ref. 20.

<sup>e</sup>The correction is defined as

$$\Delta \left[ \frac{d\sigma(0)}{d\Omega} \right]_{\text{el}} = \frac{1}{9} \{ [\langle R^2 \rangle_{\text{vib}}^2 + \frac{4}{5} \langle Q^2 \rangle_{\text{vib}}] - [\langle R^2 \rangle_{\text{vib}} + \frac{4}{5} \langle Q \rangle_{\text{vib}}^2] \},$$

where Eq. (11) is used to calculate the individual differences.

where  $q_i$  is the  $i$ th normal coordinate<sup>3</sup> and the sums are over all the normal coordinates. Note that both first-order corrections and those involving the second derivatives of  $R^2$  with respect to the  $q$ 's are treated in exactly the same way in both ways of averaging and thus cancel in the difference. In Table II the parameters used to estimate the difference for H<sub>2</sub> and N<sub>2</sub> using Eq. (11) are given with the final results for the difference between electron scattering at zero angle and the cross section estimated

from magnetic susceptibility measurements. The smallness of these results suggests, for current experimental accuracies, that direct comparisons between different experimental quantities can be made without making corrections for vibrational effects. Further, it should be possible to extract vibrationally averaged moments directly from properly corrected elastic electron scattering results. Of course, this does not mean that one can compare nonvibrationally averaged theory directly with experiment.

TABLE III. Magnetic susceptibility parameters, quadrupole moments, and mean-square radii for H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>.

Molecule	$g$	$\langle \chi_1^p \rangle_{\text{vib}} \times 10^6$ <sup>c</sup> cm <sup>3</sup> /mole	$\langle \chi \rangle_{\text{vib}} \times 10^6$ cm <sup>3</sup> /mole	$\langle \chi^d \rangle_{\text{vib}} \times 10^6$ <sup>f</sup> cm <sup>3</sup> /mole	$\langle Q \rangle_{\text{vib}}$ (a.u.)	$\langle \langle r^2 \rangle \rangle_{\text{vib}}$ <sup>k</sup> (a.u.)	$\langle \langle R^2 \rangle \rangle_{\text{vib}}$ <sup>m</sup> (a.u.)
H <sub>2</sub>	+ 0.882 91 <sup>a</sup>	+ 0.1469	- 4.0118 <sup>d</sup>	- 4.1097	+ 0.5892 <sup>g</sup> + 0.474 ± 0.034 <sup>h</sup>	5.1894	- 4.1330
N <sub>2</sub>	- 0.2593 <sup>b</sup>	+ 27.34	- 11.94 ± 0.02 <sup>d</sup>	- 30.16 ± 0.02	- 1.09 ± 0.02 <sup>i</sup>	38.09 ± 0.03	- 22.90 ± 0.03
O <sub>2</sub>	- 0.13 <sup>b</sup>		- 4240 <sup>c</sup>		- 0.29 <sup>j</sup>	~ 46 <sup>l</sup>	~ - 25

<sup>a</sup>See Ref. 21.

<sup>b</sup>See Ref. 22.

<sup>c</sup>Calculated from the equation

$$\langle \chi_1^p \rangle_{\text{vib}} = 4.2425 \times 10^{10} \cdot \langle R_e^2/2 \rangle_{\text{vib}} \left[ g \frac{M}{M_p} - Z \right] \text{ cm}^3/\text{mole}$$

where  $M/M_p$  is the ratio of the molecular mass to the proton mass and  $\langle R_e^2/2 \rangle_{\text{vib}} = (R_e^2 + 2R_e \langle q \rangle + \langle q^2 \rangle)/2$ . See Ref. 23.

<sup>d</sup>See Ref. 24.

<sup>e</sup>See Ref. 25.

<sup>f</sup> $\langle \chi^d \rangle_{\text{vib}} = \langle \chi \rangle_{\text{vib}} - \frac{2}{3} \langle \chi_1^p \rangle_{\text{vib}}$ .

<sup>g</sup>See Ref. 26.

<sup>h</sup>See Ref. 27.

<sup>i</sup>See Refs. 28 and 29.

<sup>j</sup>See Refs. 28 and 29.

<sup>k</sup> $\langle \langle r^2 \rangle \rangle_{\text{vib}} = (\langle \chi^d \rangle_{\text{vib}} \times 10^{-10})/2.828\ 34a_0^2$ .

<sup>l</sup>Average of  $\langle r^2 \rangle$  for N<sub>2</sub> from the bulk magnetic susceptibility and a value of  $\langle r^2 \rangle$  for molecular fluorine determined from an SCF calculation. See Ref. 23.

<sup>m</sup> $\langle \langle R^2 \rangle \rangle_{\text{vib}} = (Z/2) \langle R_e^2 \rangle_{\text{vib}} - \langle r^2 \rangle_{\text{vib}}$ .

If molecular  $g$  factors and molecular geometric parameters, or equivalently the paramagnetic susceptibility, along with the bulk magnetic susceptibility are known then it is possible to determine the vibrationally averaged mean-square electronic radius of the molecule,  $\langle r^2 \rangle$ . This result, coupled with a knowledge of the equilibrium molecular structure and the vibrational moments  $\langle q_i \rangle$  and  $\langle q_i q_j \rangle$ , permits the calculation of  $\langle R^2 \rangle$  in Eqs. (7)–(10). The details are given in the Appendix. If the total electric quadrupole moment is available then the elastic cross section at  $K=0$  for nonpolar molecules can be calculated. Except for certain cases, one of them being molecular oxygen which is discussed below, the cross section predicted from magnetic measurements can serve as a check on elastic electron cross-section measurements or vice versa. In Table III the parameters used to calculate the zero-angle elastic cross sections are given.

The coefficients of the terms proportional to  $K^2$  and  $K^4$  in Eqs. (7)–(10) contain some information not obtainable from other experiments that we are aware of. In the case of the coefficient of  $K^2$ , if one has an experimental value of the quadrupole or other required electric moment then it is possible to extract the  $\langle R^4 \rangle$  moment involving

the electronic moments  $\langle z^4 \rangle$ ,  $\langle r^2 z^2 \rangle$ , and  $\langle r^4 \rangle$ . Note that the term  $\langle R^2 Q \rangle$  involves two of these same electronic moments. Such terms should be extremely sensitive to the quality of any description of the molecular charge density since they place extreme weight on its outer most reaches. For a diatomic molecule with no dipole moment and with the coefficient of the  $K^2$  term designated by  $\beta$ , we have

$$\begin{aligned} & (\langle R^2 \rangle - \frac{4}{7} Q) \langle r^4 \rangle + \frac{12}{7} Q \langle r^2 z^2 \rangle \\ &= (\langle R^2 \rangle + \frac{8}{7} Q) \frac{Z \langle R_e^4 \rangle_{\text{vib}}}{8} - 90\beta, \end{aligned} \quad (12)$$

where  $R_e$  is the equilibrium internuclear distance and  $\langle R^2 \rangle$  is obtained from the zero-angle elastic scattering with the help of the quadrupole moment  $Q$ . If the hexadecapole moment,  $\Phi$ , given as

$$\frac{35}{8} \langle z^4 \rangle - \frac{30}{8} \langle r^2 z^2 \rangle + \frac{3}{8} \langle r^4 \rangle = \frac{z \langle R_e^4 \rangle_{\text{vib}}}{8} - \Phi, \quad (13)$$

is known then we have two relationships involving the three unknown quantities  $\langle z^4 \rangle$ ,  $\langle r^2 z^2 \rangle$ , and  $\langle r^4 \rangle$ . Be-

TABLE IV. A comparison of the Born elastic cross sections,  $[d\sigma(0)/d\Omega]_{\text{el}}/\gamma^2 a_0^2$ , for  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$  from electron scattering with the predictions of theory and magnetic susceptibility measurements.

Molecule	Zero-angle elastic electron scattering cross section (a.u.)	Cross section <sup>d</sup> derived from magnetic susceptibility data (a.u.)	Theory
$\text{H}_2$	$2.0 \pm 0.2^a$ (25 keV)	1.938 <sup>e</sup> 1.927 <sup>f</sup>	1.969 <sup>h</sup>
$\text{N}_2$	$47 \pm 3^b$ (37 keV) $54 \pm 2^c$ (30 keV)	$58.4 \pm 0.2$	61.28 <sup>h</sup> 66.1 <sup>i</sup>
$\text{O}_2$	$46 \pm 3^b$ (60 keV) $44 \pm 3^b$ (37 keV)	67.4 <sup>g</sup>	55.4 <sup>i</sup>

<sup>a</sup>See Table I and Ref. 14.

<sup>b</sup>See Table I and Ref. 15.

<sup>c</sup>See Table I and Ref. 16.

<sup>d</sup>Calculated from the equation

$$\left[ \frac{d\sigma(0)}{d\Omega} \right]_{\text{el}} / \gamma^2 a_0^2 = \frac{1}{9} (\langle R^2 \rangle_{\text{vib}})^2 + \frac{4}{5} \langle Q \rangle_{\text{vib}}^2$$

where the constants were obtained from Table III.

<sup>e</sup>Obtained by using the larger value for the quadrupole moment listed in Table III. The vibrational correction from Table II has been applied.

<sup>f</sup>Obtained by using the smaller value for the quadrupole moment listed in Table III. Vibrational correction in Table II has been applied.

<sup>g</sup>See comment 1 in Table III.

<sup>h</sup>Obtained from Ref. 1(e) with vibrational correction given in Table II added in the case of  $\text{H}_2$ .

<sup>i</sup>IAM theory using values of the atomic partial-wave (PW) scattering factors interpolated from the tables in Ref. 9 as

$$\left[ \frac{d\sigma(0)}{d\Omega} \right]_{\text{el}} / \gamma^2 a_0^2 = \frac{4}{\gamma^2 a_0^2} |f_{\text{PW}}(0)|^2.$$

These have been included to show the trend going from  $\text{N}_2$  to  $\text{O}_2$ .

cause  $Q$  is usually small compared to  $\langle R^2 \rangle$ , Eq. (12) can be used to determine an estimate of  $\langle r^4 \rangle$ . Equation (13) can then be used to set bounds on possible values of the other two moments.

**Hydrogen.** The results for  $H_2$  from the elastic experiments of Geiger<sup>14</sup> at 25 keV matched to the absolute measurements of Ulsh *et al.*<sup>30</sup> at the same energy were used to obtain an estimate of the cross section at  $K=0$ . The data were not judged to be of sufficient quality to attempt a least-squares fit to extract information on the other coefficients. The results are in excellent agreement with those obtained from magnetic susceptibility measurements and theory as shown in Table IV. In Table V, values for the electronic moments  $\langle x^2 \rangle$ ,  $\langle z^2 \rangle$ , and  $\langle r^2 \rangle$ , and the diamagnetic susceptibility are given. Again the agreement is excellent. Note that these moments depend heavily on the nuclear contribution which is known very accurately. Hence to measure  $\langle r^2 \rangle$ , for example, to 1% accuracy only requires an accuracy in the elastic cross-section measurement of about 4%.

**Nitrogen.** Here the situation is less clear. The results of Fink and Kessler<sup>15</sup> using 37 keV electrons yield an estimate 17% below the magnetic susceptibility result while recent, more precise measurements, by Fink and Coffman<sup>16</sup> lie about 7% below the magnetic susceptibility result. The best theoretical estimate to date, based on a wave function giving 24% of the correlation energy, is 5% above the susceptibility derived result,<sup>1(e)</sup> but studies on wave function quality strongly suggest that the

theoretical result will decrease as the wave function undergoes further improvements.<sup>1(e)</sup> All results are included in Tables IV and V. It should be pointed out that the 2.4% difference between the  $r^2$  values derived from the scattering and magnetic susceptibility measurements could conceivably be the result of oxygen contamination in the susceptibility measurements. If one assumes that the more recent molecular  $g$  value for  $N_2$  is accurate and that the 2.4% difference is due to an error in the older bulk magnetic susceptibility measurement then that result would have been in error by 6%. The amount of oxygen impurity necessary to cause such an error would only be 0.018% which might have been beyond the detection limits at the time the susceptibility measurement was made.

In the case of the latest results by Fink and Coffman,<sup>16</sup> the data precision was judged of sufficient quality to attempt a least-squares fit of the small angle data [ $0.25 < K$  (a.u.)  $< 2.1$ ]. The results for  $\beta$  and  $\gamma$  were  $-36 \pm 4$  and  $+12 \pm 4$  which can be compared with Liu's<sup>1(e)</sup> best theoretical results of  $-53$  and  $+26$ . Continued efforts are underway to improve the electron results. Based on the percent of the correlation energy and the rate of convergence exhibited by the wave functions investigated by Liu,<sup>1(e)</sup> it appears that our experimental  $\beta$  value may be too low but the  $\gamma$  value lies in a region to which convergence could conceivably take place. Clearly further calculations with more highly correlated wave functions are desirable.

**Oxygen.** Here, because of the enormous size of the bulk

TABLE V. Values of  $\langle r^2 \rangle$ ,  $\langle z^2 \rangle$ ,  $\langle x^2 \rangle$ , and the diamagnetic susceptibility obtained from Born zero-angle elastic electron cross sections and quadrupole moment measurements.

Molecule	Source (for details see Tables III and IV)	$\langle r^2 \rangle$ (a.u.) <sup>a</sup>	$\langle z^2 \rangle$ (a.u.) <sup>b</sup>	$\langle x^2 \rangle$ (a.u.) <sup>c</sup>	$\chi^d$ (cm <sup>3</sup> /mole) <sup>d</sup>
					$\times 10^6$
H <sub>2</sub>	25 keV electrons	5.2±0.2	2.05	1.58±0.07	-4.1±0.2
	magnetic-susceptibility	5.189	2.041	1.574	-4.1097
	theory	5.223	2.053	1.585	-4.136
N <sub>2</sub>	37 keV electrons	35.7±0.7	22.8±0.2	6.5±0.2	-28.3±0.6
	30 keV electrons	37.2±0.4	23.3±0.1	7.0±0.1	-29.4±0.3
	magnetic-susceptibility	38.09	23.55	7.27	-30.16±0.02
	theory	38.66	23.74	7.46	-30.62
	IAM theory	39.56	24.04	7.76	-31.33
O <sub>2</sub>	60 keV electrons	41.4±0.7	28.0±0.2	6.7±0.2	-32.8±0.6
	37 keV electrons	41.0±0.7	27.9±0.2	6.5±0.2	-32.5±0.6
	37 keV electrons	43.3	28.7	7.3	-34.3
	(scaled)				
	$\langle r^2 \rangle$ estimated	46	29.6	8.2	-36
	IAM theory	43.4	28.7	7.3	-34.4
	HF theory (Ref. 31)	43.353	28.524	7.414	-34.331

$${}^a\langle r^2 \rangle = Z \langle R_e^2 \rangle_{\text{vib}} / 2 - \langle \langle R^2 \rangle \rangle_{\text{vib}}, \quad \langle \langle R^2 \rangle \rangle_{\text{vib}} = \left[ 9 \left[ \frac{d\sigma(0)}{d\Omega} \right]_{\text{el}} / \gamma^2 a_0^2 - \frac{4}{3} \langle Q \rangle_{\text{vib}}^2 \right]^{1/2}.$$

$${}^b\langle z^2 \rangle = \frac{1}{3} (\langle r^2 \rangle + 2Q_e), \quad Q_e = -\langle Q \rangle_{\text{vib}} \quad \frac{Z}{2} \langle R_e^2 \rangle_{\text{vib}} = \langle z^2 \rangle - \langle x^2 \rangle.$$

$${}^c\langle x^2 \rangle = \langle z^2 \rangle - Q_e.$$

$${}^d\chi^d = -0.79193 \times 10^{-6} [\langle r^2 \rangle \text{ (a.u.)}] \text{ cm}^3/\text{mole}.$$

magnetic susceptibility and its paramagnetic contribution, it has not been possible to extract an estimate of the diamagnetic susceptibility. The only available experimental value of  $\langle r^2 \rangle$  appears to be an estimate which was obtained by averaging the  $N_2$  experimental value with a self-consistent field (SCF) theoretical prediction for molecular fluorine.<sup>23</sup> Two absolute experimental measurements of the small angle behavior of the elastic cross section of  $O_2$  at 37 and 60 keV have been reported by Fink and Kessler.<sup>15</sup> Their value for 60 keV,  $45 \pm 2$  a.u., is slightly larger than their 37 keV value of  $43 \pm 2$  a.u. Because all corrections are reduced by increasing the incident electron energy ( $\gamma^2$  excepted), we may regard the 60 keV data as being the more accurate of the two. Both values lie below the  $N_2$  result obtained by the same authors using identical experimental conditions. As observed in the previous discussion of  $N_2$  results, these measurements appear to be low. Presumably this is due to some unknown source of systematic error. On the other hand, the trend suggested by the data, that  $(d\sigma/d\Omega)_{el}/\gamma^2 a_0^2$  at  $\theta=0^\circ$  for  $O_2$  is less than the  $N_2$  cross section value, is believed to be accurate. The semiempirical estimate on the other hand predicts a value of 69 a.u., which is significantly larger than the magnetic susceptibility result of 58 a.u. for  $N_2$ . The IAM model prediction, which is usually a reliable indication of trends, yields 66 a.u. for  $N_2$  and 55 a.u. for  $O_2$ , a definite contraction. In Tables IV and V, the results are summarized. In Table V the electronic moment values are also given using the electron scattering value for  $O_2$  obtained by scaling the 37 keV electron scattering values for  $O_2$  and  $N_2$  from the Fink-Kessler<sup>15</sup> experiments to the magnetic susceptibility results for  $1/\gamma^2 a_0^2 (d\sigma/d\Omega)_{el}$  obtained for  $N_2$ . These results are compared to the semiempirical results of Flygare *et al.*<sup>23</sup> We feel that the results derived from the Fink-Kessler<sup>15</sup> rescaled values are more accurate than previously published values since they are consistent with a contraction of the zero-angle elastic cross section relative to  $N_2$  while the other results are not. Note that  $|\langle R^2 \rangle|$  and not  $\langle r^2 \rangle$ , follow the trend exhibited by the  $\langle r^2 \rangle$  values for the atoms N and O. The mean-square molecular electronic radius,  $\langle r^2 \rangle$ , exhibits an increase in value in going from  $N_2$  to  $O_2$ . Our conclusions are supported by an unpublished theoretical calculation by Liu<sup>31</sup> who used a near-Hartree-Fock wave function which gave an excellent value ( $\pm 4\%$ ) of the quadrupole moment. It should be noted that this is not the case for  $N_2$  where HF values of the quadrupole moment are in error by 14%. Liu's values are given in Table V.

We have shown that state-of-the-art absolute small-angle elastic electron scattering measurements are capable of yielding direct information on certain moments of molecular electronic charge densities when such measurements are combined with experimental values of electric moments and a precise knowledge of molecular structure parameters. This approach does not involve any assumptions as to the form of the molecular electron charge density. For nonpolar molecules the zero-angle intercept of the absolute elastic cross section yields information on the mean-square radius of the electron charge density which when used with quadrupole moment data allows the deter-

mination of the mean-square distance parallel,  $\langle z^2 \rangle$  and perpendicular,  $\langle x^2 \rangle$ , to the major molecular symmetry axis. These values make it possible to predict the diagonal elements of the diamagnetic susceptibility tensor. Because the electron scattering experiments measure the difference between nuclear and electronic quantities and since the nuclear quantities, molecular structure parameters, are usually precisely known, one has a particularly sensitive method for obtaining moments of the electronic charge distribution. The relative error in the mean-square radius is generally about  $\frac{1}{4}$  of the error involved in establishing the zero-angle value of the elastic scattering. While for some molecular symmetries a knowledge of the quadrupole moment is required to obtain an accurate estimate of the mean-square radius, the quadrupole-dependent contribution is normally less than 1% and can be neglected as a first approximation.

If the bulk magnetic susceptibility is known and the paramagnetic contribution can be calculated then reliable values for the Born zero-angle elastic limit can be computed. These can serve as a valuable check on the determination of the absolute intensity scale in the scattering experiment. The angular dependence of the small-angle absolute elastic cross section yields data on certain higher moments of the electronic charge density. A preliminary study on recently obtained elastic data for  $N_2$  shows promise of yielding useful results on the higher moments of the electronic charge density such as  $\langle r^4 \rangle$  and  $\langle r^6 \rangle$ . Data on  $\langle r^4 \rangle$  can be combined with measured values of the hexadecapole moment to obtain constraints on the allowed values of the three independent fourth-order electronic moments  $\langle r^4 \rangle$ ,  $\langle z^4 \rangle$ , and  $\langle z^2 r^2 \rangle$ .

As suggested by the work of Lassette<sup>32</sup> on inelastic scattering, it may be advantageous to least-squares fit the small-angle elastic scattering corrected for all non-first-Born effects, to a function of the form

$$\left[ \frac{d\sigma}{d\Omega} \right]_{el} / \gamma^2 a_0^2 = \sum_{n=1}^M \frac{\alpha_n (K/\beta_n)^{2n-2}}{\left[ 1 + \left[ \frac{K}{\beta_n} \right]^2 \right]^{n+1}} \quad (14)$$

which is more closely tailored to the actual cross-section shape than a straight power-series expansion. Once a fit of the above form has been obtained, it is a simple matter to relate the coefficients in a power series of the form  $\alpha + \beta K^2 + \gamma K^4 \dots$  with the  $\alpha_n, \beta_n$  parameters as

$$\alpha = \alpha_1, \beta = -(2\alpha_1/\beta_1^2 - \alpha_2/\beta_2^2) \quad (15)$$

and

$$\gamma = 3\alpha_1/\beta_1^4 - 3\alpha_2/\beta_2^4 + \alpha_3/\beta_3^4.$$

Note that  $\alpha$ ,  $\beta$ , and  $\gamma$  depend only on a knowledge of the first three terms in Eq. (14).

Finally, it is worth mentioning that the results presented here are equally valid for small-angle elastic x-ray scattering in the Born approximation providing all nuclear terms are set equal to zero. With x rays, moments of the electronic charge density can be obtained directly.

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APPENDIX: FORMULAS FOR THE CALCULATION OF  $[d\sigma(0)/d\Omega]_{el}$  FROM MAGNETIC SUSCEPTIBILITY DATA

The formulas necessary to transform bulk magnetic susceptibility measurements to the zero-angle elastic electron scattering cross section have been collected together and are presented below. The bulk susceptibility,  $\chi$ , is given as the average of the trace of the susceptibility tensor as

$$\chi = \frac{1}{3}(\chi_{xx} + \chi_{yy} + \chi_{zz}), \quad (A1)$$

where each diagonal element is a sum of a diamagnetic,  $\chi_{xx}^d$ , and a paramagnetic,  $\chi_{xx}^p$ , contribution. The diamagnetic contribution is the one of interest here since it depends on the electronic moment  $\langle r^2 \rangle$ . However since it is not a directly measurable quantity it is first necessary to determine the paramagnetic contribution. The total diamagnetic contribution and the diagonal components of the paramagnetic contributions can be written as

$$\chi^d = -\frac{Ne^2}{2mc^2} \langle r^2 \rangle \quad (A2)$$

and

$$\chi_{xx}^p = -\frac{Ne^2}{4mc^2} \left[ \frac{g_{xx} I_{xx}}{M_p} - \sum_n Z_n (R_n^2 - X_n^2) \right], \quad (A3)$$

where  $Ne^2/4mc^2 = 4.2425 \times 10^{10}$  cgs units,  $g_{xx}$  is the molecular  $g$  factor in the  $x$  direction,  $I_{xx}$  is the  $x$  component of the moment of inertia,  $M_p$  is the proton rest mass, and  $X_n$  is the projection of  $R_n$  onto the  $x$  direction. The  $y$  and  $z$  diagonal elements of  $\chi^p$  are similarly defined.

In order to calculate  $[d\sigma(0)/d\Omega]_{el}$  one must obtain the necessary molecular  $g$  values and structural parameters needed to calculate the elements of  $\chi^p$  by use of Eq. (A3). Next,  $\chi^d$  is obtained from Eq. (A1), with the knowledge of  $\chi^p$ . Finally Eq. (A2) is used to obtain the electronic average  $\langle r^2 \rangle$ . From this and the structural parameters,  $\langle R^2 \rangle_{vib}$  can be calculated by means of Eq. (4) since  $\langle R^2 \rangle_{vib} = \langle Q_{00}^2 \rangle_{vib}$ . Assuming the molecule has no permanent dipole moment and that the quadrupole moment is known, one then calculates  $\frac{1}{9}(\langle R^2 \rangle_{vib}^2 + \frac{4}{3}\langle Q \rangle_{vib})$  to which the vibrational correction discussed in Eq. (11) must be added in the form

$$\frac{1}{9} \left[ \sum_i \sum_j \left( \frac{\partial \langle R^2 \rangle}{\partial q_i} \frac{\partial \langle R^2 \rangle}{\partial q_j} + \frac{4}{5} \frac{\partial Q}{\partial q_i} \frac{\partial Q}{\partial q_j} \right) (\langle q_i q_j \rangle - \langle q_i \rangle \langle q_j \rangle) \right].$$

This final result can then be compared with experimental values of  $[d\sigma(0)/d\Omega]_{el}/\gamma^2 a_0^2$  which have been suitably corrected to the Born limit.

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using the tensor two-index contraction null equalities.

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$$F^0(\mathbf{r}) = (2e^{ik_0 r}/r) \{ [Z - F_x(s)(1 - s^2/2k_0^2)]/s^2 \}.$$

Note that in addition a factor of  $\frac{1}{2}$  was omitted from the exchange term. See Ref. 1(d). The factor of  $\frac{1}{2}$  is also missing in the discussion on exchange in Ref. 2.

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