

Compton profiles and other momentum-space properties of  $N_2$ 

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Various momentum-space properties of  $N_2$  in its ground electronic state ( $X^1\Sigma_g^+$ ) are computed from a wave function substantially more accurate than those previously used for such purposes. The wave function was obtained by first-order configuration interaction (CI) relative to a full valence multiconfiguration self-consistent-field reference wave function constructed from a large basis set of Slater-type functions. The calculated isotropic Compton profile agrees best with 160-keV  $\gamma$ -ray experiments and with a previous CI calculation. The calculated values of  $\langle p^k \rangle$  ( $-2 \leq k \leq 4$ ) agree well with values obtained from 25-keV electron-impact experiments. The value and second derivative of the spherically averaged momentum density at  $p=0$  are not quite as sensitive to details of electron correlation as had been thought previously. Anisotropic properties such as directional Compton profiles parallel and perpendicular to the bond and the  $J(0, \gamma)$  surface are also calculated; however, calculations with a larger basis set will be required to obtain converged values of these anisotropic properties.

## I. INTRODUCTION

Electron momentum distributions (EMD's) in atoms, molecules, and solids have been the focus of much research during the past 20 years.<sup>1</sup> EMD's have been studied with many techniques including x-ray and  $\gamma$ -ray Compton scattering,<sup>2</sup> positron annihilation,<sup>3</sup> high-energy electron-impact spectroscopy,<sup>4</sup> binary ( $e, 2e$ ) spectroscopy,<sup>5</sup> and quantum-mechanical calculations.<sup>6,7</sup>

The EMD of the nitrogen molecule  $N_2$  in its ground ( $X^1\Sigma_g^+$ ) electronic state has been studied repeatedly by experimental<sup>8-17</sup> and theoretical<sup>7,10,16-32</sup> methods. The first measurements of the spherically averaged or isotropic Compton profile (ICP) of  $N_2$  were made with x rays by Kappeler<sup>8</sup> in 1936, and with electrons by Hughes and Starr<sup>9</sup> in 1939. More recent experimental work<sup>10-17</sup> on  $N_2$  carried out during the 1970's spans almost the entire range of techniques available. The first theoretical study of the EMD of  $N_2$  was a calculation of the ICP by Duncan<sup>18</sup> in 1943. During the past 15 years, there have been numerous calculations of momentum-space properties of  $N_2$  including the ICP,<sup>10,20-25,28,29,31</sup> radial orbital EMD's,<sup>16,17,29</sup> the directional Compton profiles (DCP's) parallel and perpendicular to the molecular axis,<sup>23-25,29,31</sup> the three-dimensional EMD,<sup>7,19,21,22,24,26,29,30</sup> the partial waves of the EMD,<sup>7,27</sup> and the anisotropy of the kinetic energy tensor.<sup>27,29,32</sup> These calculations have been made using a variety of self-consistent-field<sup>18,23,30,33-37</sup> (SCF) and configuration interaction<sup>23,38</sup> (CI) wave functions, as well as the Hartree-Fock-Slater method<sup>29</sup> and some other density-functional approaches.<sup>28,31</sup>

The purpose of this paper is to report a calculation of the ICP, DCP's, and other momentum-space properties of  $N_2$  using a CI wave function that is substantially more accurate than those used in previous calculations of this nature. Moreover, the results reported for some momentum-space properties are to our knowledge, the first correlated ones ever calculated for  $N_2$ . Methodological details can be found in Sec. II. Results for properties of the isotropic EMD are presented and compared with experiment in Sec. III. Properties that depend upon the anisotropy of the EMD are presented and discussed in Sec. IV. Concluding remarks may be found in Sec. V.

## II. METHODOLOGICAL DETAILS

## A. Review of theory

Hartree atomic units<sup>39</sup> are used throughout this paper. The momentum density for an  $N$ -electron molecule in a state described by the position-space wave function  $\psi$  is given by<sup>40</sup>

$$\Pi(\mathbf{p}) = (2\pi)^{-3} \int \exp(i\mathbf{p} \cdot \mathbf{r}) \Gamma^{(1)}(\mathbf{s} | \mathbf{s} + \mathbf{r}) d\mathbf{s} d\mathbf{r} \quad (1)$$

in which  $\Gamma^{(1)}$  is the position-space representation of the spin-traced one-electron reduced density operator defined by

$$\Gamma^{(1)}(\mathbf{s} | \mathbf{r}) = N \int \psi^*(\mathbf{r}\sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \times \psi(\mathbf{s}\sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_N) d\sigma_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N, \quad (2)$$

where  $\mathbf{x}_j = (\mathbf{r}_j, \sigma_j)$  is a combined space-spin coordinate for electron  $j$ . Within the impulse approximation,<sup>1</sup> the directional Compton profile (DCP) can be obtained from the momentum density as follows:<sup>41</sup>

$$J(q, \mathbf{q}/q) = \int \Pi(\mathbf{p}) \delta(\mathbf{p} \cdot \mathbf{q}/q - q) d\mathbf{p}. \quad (3)$$

The isotropic Compton profile (ICP) is simply the spherical average of the DCP; thus,

$$\bar{J}(q) = (4\pi)^{-1} \int \bar{J}(q, \mathbf{q}/q) d\Omega_{\mathbf{q}/q} \quad (4a)$$

$$= 2\pi \int_0^\infty \Pi_0(p) p dp \quad (4b)$$

in which  $\Pi_0$  is the spherical average of the EMD given by

$$\Pi_0(p) = (4\pi)^{-1} \int \Pi(\mathbf{p}) d\Omega_{\mathbf{p}}. \quad (5)$$

Other isotropic properties of interest are the moments

$$\langle p^k \rangle = \int \Pi(\mathbf{p}) p^k d\mathbf{p} = 4\pi \int_0^\infty \Pi_0(p) p^{k+2} dp, \quad -3 < k < 5 \quad (6a)$$

where the limits on  $k$  arise from the  $p^{-8}$  asymptotic behavior<sup>42</sup> of  $\Pi_0(p)$  and the fact that  $\Pi_0$  is finite and nonzero at  $p=0$ . These moments can also be obtained directly from  $\bar{J}(q)$ . Thus,<sup>42-44</sup>

$$\langle p^k \rangle = 2(k+1) \int_0^\infty \bar{J}(q) q^k dq, \quad 0 \leq k \leq 4 \quad (6b)$$

$$\langle p^{-1} \rangle = 2\bar{J}(0), \quad (6c)$$

and<sup>45</sup>

$$\langle p^{-2} \rangle = 2 \int_0^\infty q^{-2} [\bar{J}(0) - \bar{J}(q)] dq. \quad (6d)$$

Since experimental measurements of the ICP are most accurate near  $q=0$ , the coefficients of its MacLaurin expansion

$$\bar{J}(q) = \langle p^{-1} \rangle / 2 - \pi \Pi_0(0) q^2 - [\pi \Pi_0''(0) / 4] q^4 + \dots \quad (7)$$

are of interest as well.

In a linear molecule, the EMD has  $D_{\infty h}$  symmetry.<sup>7</sup> Thus, if the polar axis is chosen to be the molecular axis, the EMD and DCP are independent of the azimuthal angle, and

$$\Pi(\mathbf{p}) = \Pi(p, \theta_p) \quad (8)$$

and

$$J(q, \mathbf{q}/q) = J(q, \gamma) \quad (9)$$

in which  $\theta_p$  and  $\gamma$  are the polar angles corresponding to  $\mathbf{p}$  and  $\mathbf{q}$ , respectively. The DCP's parallel ( $\gamma=0$ ) and perpendicular ( $\gamma=\pi/2$ ) to the molecular axis are of the most interest. Moreover, the so-called  $J(0, \gamma)$  surface<sup>24,25</sup> is often used as a convenient probe of the anisotropy of the EMD. Another method advocated for the study of the anisotropy is the partial-wave decomposition:<sup>7,27,46</sup>

$$\begin{aligned} \Pi(p, \theta_p) = & \Pi_0(p) + \Pi_2(p) P_2(\cos\theta_p) \\ & + \Pi_4(p) P_4(\cos\theta_p) + \dots \end{aligned} \quad (10)$$

in which the  $P_L$  are Legendre polynomials,  $\Pi_0(p)$  is the spherically averaged EMD of Eq. (5), and the higher par-

tial waves  $\Pi_2, \Pi_4, \dots$  determine the anisotropy. A quantitative measure which is of great chemical interest<sup>27,29,32,47,46</sup> is the anisotropy of the kinetic energy tensor given by

$$\Delta T \equiv \langle p_z^2 - p_x^2 \rangle / 2 = \langle p^2 P_2(\cos\theta_p) \rangle / 2 \quad (11a)$$

$$= (2\pi/5) \int_0^\infty p^4 \Pi_2(p) dp \quad (11b)$$

$$= \int_0^\infty [J(q, 0) - J(q, \pi/2)] q^2 dq. \quad (11c)$$

## B. Computations

The momentum-space properties defined in Sec. II A were calculated for the  $N_2$  molecule in its electronic ground state ( $X^1\Sigma_g^+$ ) at an internuclear separation of  $R=2.068a_0$  which is an older experimental estimate<sup>48(a)</sup> of the equilibrium value. The discussion in Sec. V shows that use of the more recent experimental value<sup>48(b)</sup> of  $2.074a_0$  would not affect the results appreciably. The older value has been used in this work for consistency with previous calculations.

The wave function was constructed, using the AL-CHEMY program system,<sup>49</sup> from a one-particle basis set of  $(4s, 4p, 2d)$  atom-centered Slater-type functions (STF's) obtained by starting with the  $(4s, 3p)$  "nominal" basis set of Bagus *et al.*<sup>50</sup> and adding two  $3d$  polarization STF's with exponents 2.9 and 1.3 as well as a diffuse  $2p$  STF (exponent 0.889) which minimizes the SCF energy of  $N^-$ . The SCF energy of  $N_2$  in this basis is  $-108.98093E_h$  which is comparable to the near Hartree-Fock (NHF) value of  $-108.993E_h$  obtained by Cade and Wahl.<sup>36</sup> A preliminary full valence (or complete active space) multiconfiguration SCF (MCSCF) wave function consisting of 18 many-particle configuration state functions (CSF's) was constructed; its energy was  $-109.08243E_h$ . Then a first-order<sup>51</sup> (FO) CI calculation relative to the MCSCF function was carried out to obtain the final MCSCF-FOCI wave function which contains 482 CSF's and corresponds to an energy of  $-109.12726E_h$ . This energy corresponds to a dissociation energy of 8.87 eV which is 0.9 eV less than the experimental value<sup>48(b)</sup> of 9.759 eV. The MCSCF-FOCI wave function has recovered most of the correlation energy involving the  $\pi_g$  space, and the remaining deficiencies are in the inner shells.

The MCSCF-FOCI wave function is substantially more accurate than the best one used in previous momentum-space studies of  $N_2$ —the CI wave function (energy is  $-109.108E_h$ ) constructed by Tawil and Langhoff<sup>23</sup> from a double- $\xi$  ( $2\xi$ ) basis set of Gaussian lobe functions (GLF's). Further refinements of the MCSCF-FOCI wave function are not expected to have significant effects on the ICP. This claim is supported by (i) previous studies<sup>25,52</sup> which suggest that the extended STF basis used in this work should be quite accurate for momentum-space properties, and (ii) a careful study of Brown and Smith<sup>53</sup> which indicates that a first-order<sup>51</sup> CI wave function accounts for most of the significant effects of electron correlation on the EMD.

The MCSCF-FOCI wave function has already been used to compute cross sections for the elastic scattering of high-energy ( $>1000$  eV) electrons.<sup>54(a)</sup> Moreover, an entirely analogous wave function for  $R=2.074a_0$  has been

used to compute elastic cross sections for the scattering of low-energy (1.5–30 eV) electrons from gaseous nitrogen.<sup>54(b)</sup> The calculations of the momentum-space properties from the MCSCF-FOCI wave function were carried out in a standard manner.<sup>41</sup>

### III. ISOTROPIC PROPERTIES: COMPARISON WITH EXPERIMENT

#### A. Isotropic Compton profile

Table I lists the values of  $\bar{J}(q)$  and  $\Pi_0(p)$  computed from the MCSCF-FOCI wave function. Note that more significant figures than warranted by the accuracy of the wave function and the impulse approximation have been given in order to facilitate interpolation.

A comparison with experiment is presented in Table II and Fig. 1. Typical experimental uncertainties in the ICP's obtained by photon scattering are 1% of  $\bar{J}(0)$  or  $\pm 0.05$ . The root mean square (rms) deviations, based on points with  $q \leq 5$ , show that the ICP obtained by 25-keV electron-impact experiments<sup>15</sup> differs from the present calculation by much more than any of the photon scattering<sup>11–14</sup> ICP's. The  $\gamma$ -ray<sup>12–14</sup> ICP's have smaller rms

deviations from the MCSCF-FOCI results than the average<sup>11,12</sup> of the Ag  $K\alpha$  (22.16 keV) and the Mo  $K\alpha$  (17.34 keV) x-ray ICP's. As in the case<sup>55</sup> of Kr, the original 160-keV  $\gamma$ -ray ICP reported by Eisenberger and Reed<sup>12</sup> is in closer agreement with the best calculation than the ICP obtained by reanalysis<sup>13</sup> of the data using a new relativistic relationship between the  $\gamma$ -ray cross section and the ICP. Ribberfors<sup>56</sup> has since developed a more accurate relationship between the  $\gamma$ -ray cross section and the ICP. It would be interesting to see the ICP's obtained by a reanalysis of the  $\gamma$ -ray data<sup>12</sup> using Ribberfors's iterative procedure<sup>56</sup> even though his analysis suggests that only small differences can be expected for data collected at a scattering angle of  $173^\circ$  as it was in Eisenberger and Reed's experiment.<sup>12</sup>

A comparison with previous calculations is presented in Table II and Fig. 2. The ICP (Refs. 10 and 20) calculated from a minimal STF basis SCF wave function,<sup>34</sup> and the ICP (Refs. 21, 22, and 24) computed from a minimal STF basis full valence CI wave function<sup>38</sup> are not shown because they are not very accurate; their rms deviations (for  $q \leq 5$ ) from the MCSCF-FOCI results amount to 1.7% and 2.4% of  $\bar{J}(0)$ , respectively. The smaller rms deviation for the  $2\xi$ -SCF  $\bar{J}(q)$  as compared with that for the

TABLE I. Isotropic and directional Compton profiles and the spherically averaged momentum density for  $N_2$  computed from the MCSCF-FOCI wave function.

$q$	$\Pi_0(q)$	$\bar{J}(q)$	$J(q,0)$	$J(q,\pi/2)$
0.0	1.320 59	5.261 96	5.745 19	5.315 60
0.1	1.306 70	5.220 69	5.666 09	5.273 75
0.2	1.268 17	5.099 38	5.440 92	5.150 13
0.3	1.211 13	4.904 75	5.101 35	4.950 22
0.4	1.139 35	4.646 42	4.688 17	4.682 85
0.5	1.053 34	4.336 55	4.241 58	4.360 40
0.6	0.953 61	3.989 93	3.795 18	3.998 94
0.7	0.843 48	3.623 27	3.373 10	3.617 03
0.8	0.729 05	3.253 32	2.989 45	3.233 33
0.9	0.617 13	2.894 68	2.649 65	2.863 94
1.0	0.513 37	2.558 34	2.352 89	2.520 70
1.2	0.342 18	1.976 61	1.870 25	1.936 75
1.4	0.221 59	1.525 05	1.500 65	1.494 16
1.6	0.141 94	1.189 53	1.212 81	1.171 84
1.8	0.091 01	0.945 90	0.987 82	0.940 29
2.0	0.058 97	0.770 49	0.813 01	0.773 29
2.2	0.038 98	0.643 74	0.677 96	0.650 98
2.4	0.026 54	0.550 73	0.573 55	0.559 27
2.6	0.018 77	0.480 67	0.492 23	0.488 54
2.8	0.013 85	0.426 06	0.428 17	0.432 29
3.0	0.010 66	0.381 86	0.377 15	0.386 20
3.5	0.006 41	0.298 30	0.288 45	0.298 85
4.0	0.004 35	0.236 31	0.232 65	0.235 21
4.5	0.003 09	0.187 40	0.191 11	0.186 05
5.0	0.002 22	0.148 32	0.154 58	0.147 29
6.0	0.001 15	0.092 68	0.093 75	0.092 38
7.0	0.000 61	0.058 31	0.057 32	0.058 23
8.0	0.000 33	0.037 16	0.037 61	0.037 10
9.0	0.000 18	0.024 02	0.024 27	0.023 99
10.0	0.000 10	0.015 78	0.015 61	0.015 77
15.0	0.000 01	0.002 51	0.002 53	0.002 51

NHF calculation is fortuitous. The close agreement between the  $2\xi$ -CI and MCSCF-FOCI profiles supports the contention that further improvement of the MCSCF-FOCI wave function will not significantly affect the ICP.

The quantity  $\bar{J}_{\text{MCSCF-FOCI}} - \bar{J}_{\text{NHF}}$  differs substantially from  $\bar{J}_{2\xi\text{-CI}} - \bar{J}_{2\xi\text{-SCF}}$  for  $q \leq 0.5$ , although the two are

quite similar for larger  $q$ . Thus, the hybrid estimate

$$\bar{J}_H \simeq \bar{J}_{2\xi\text{-CI}} - \bar{J}_{2\xi\text{-SCF}} + \bar{J}_{\text{NHF}} \quad (12)$$

obtained by Langhoff<sup>57</sup> is much less accurate than  $\bar{J}_{2\xi\text{-CI}}$  for small  $q$ . In fact, the rms deviation ( $q \leq 5$ ) of  $\bar{J}_H$  from the MCSCF-FOCI results is 0.021, or 0.4% of  $\bar{J}(0)$ ,

TABLE II. Experimental and theoretical isotropic Compton profiles for molecular nitrogen. rms deviations are relative to column i and include points up to  $q=5$  only. The last row corresponds to rms deviations expressed as a percentage of  $\bar{J}(0)=5.262$ .

$q$	Experiment					Theory				
	a	b	c	d	e	f	g	h	i	
0.0	5.399	5.327	5.271	5.325	5.254	5.287	5.259	5.344	5.262	
0.1	5.229	5.277	5.228	5.282	5.210	5.250	5.220	5.300	5.221	
0.2	5.217	5.142	5.100	5.153	5.087	5.137	5.106	5.171	5.099	
0.3	4.906	4.924	4.896	4.947	4.881	4.951	4.919	4.963	4.905	
0.4	4.667	4.631	4.627	4.676	4.606	4.698	4.665	4.690	4.646	
0.5	4.189	4.286	4.309	4.354	4.278	4.388	4.357	4.365	4.337	
0.6	3.916	3.914	3.959	4.000	3.919	4.034	4.007	4.005	3.990	
0.7	3.460	3.523	3.593	3.630	3.547	3.657	3.637	3.629	3.623	
0.8	3.186	3.153	3.227	3.259	3.180	3.274	3.262	3.252	3.253	
0.9	2.785	2.803	2.874	2.901	2.838	2.904	2.899	2.888	2.895	
1.0	2.374	2.476	2.545	2.568	2.526	2.557	2.560	2.547	2.558	
1.1				2.266						
1.2	1.858	1.934	1.982	1.997	1.978	1.963	1.976	1.959	1.977	
1.3				1.762						
1.4	1.408	1.527	1.550	1.559	1.532	1.507	1.525	1.504	1.525	
1.5				1.384						
1.6	1.119	1.230	1.230	1.234	1.193	1.170	1.187	1.168	1.190	
1.7				1.104						
1.8	0.861	0.997	0.989	0.991	0.955	0.925	0.940	0.927	0.946	
1.9				0.892						
2.0	0.720	0.821	0.805	0.805	0.785	0.749	0.762	0.755	0.770	
2.2				0.664				0.631	0.644	
2.4								0.541	0.551	
2.5	0.475	0.542	0.524	0.521	0.544	0.499	0.505			
2.6								0.473	0.481	
2.8								0.420	0.426	
3.0	0.363	0.390	0.400	0.396	0.397	0.376	0.379	0.377	0.382	
3.5	0.249	0.301	0.299	0.295	0.310	0.297	0.298	0.295	0.298	
4.0	0.173	0.244	0.238	0.234	0.237	0.235	0.236	0.234	0.236	
4.5	0.154							0.186	0.187	
5.0	0.109		0.147	0.143	0.144	0.148	0.148	0.148	0.148	
6.0			0.086	0.083	0.098		0.093	0.093	0.093	
7.0			0.048	0.046			0.058	0.058	0.058	
8.0			0.030	0.029			0.037	0.037	0.037	
9.0			0.019	0.018			0.024	0.024	0.024	
10.0			0.009	0.008			0.016	0.016	0.016	
15.0			0.000	0.005			0.003	0.003	0.003	
rms	0.095	0.057	0.023	0.032	0.037	0.028	0.009	0.033	0.000	
rms (%)	1.81	1.09	0.43	0.61	0.70	0.53	0.18	0.63	0.00	

<sup>a</sup>25-keV electron-impact ( $12^\circ$ ) results (Ref. 15).

<sup>b</sup>Average of Ag  $K\alpha$  and Mo  $K\alpha$  x-ray scattering results of Ref. 11 as listed in Ref. 12.

<sup>c</sup>160 keV  $\gamma$ -ray scattering results of Ref. 12.

<sup>d</sup>160 keV  $\gamma$ -ray scattering results of Ref. 12 as reanalyzed in Ref. 13.

<sup>e</sup>60 keV  $\gamma$ -ray scattering results of Ref. 14.

<sup>f</sup>Calculated from a SCF wave function in a double- $\zeta$  quality basis set of Gaussian lobe functions. Reference 23.

<sup>g</sup>Calculated from a CI wave function in the basis set described in *f* above. Reference 23.

<sup>h</sup>Calculated in Ref. 25 from a near Hartree-Fock quality wave function (Ref. 35). Note that some of these values differ in the third decimal place from the ones in Refs. 12 and 20.

<sup>i</sup>Present work. Calculated from the MCSCF-FOCI wave function.

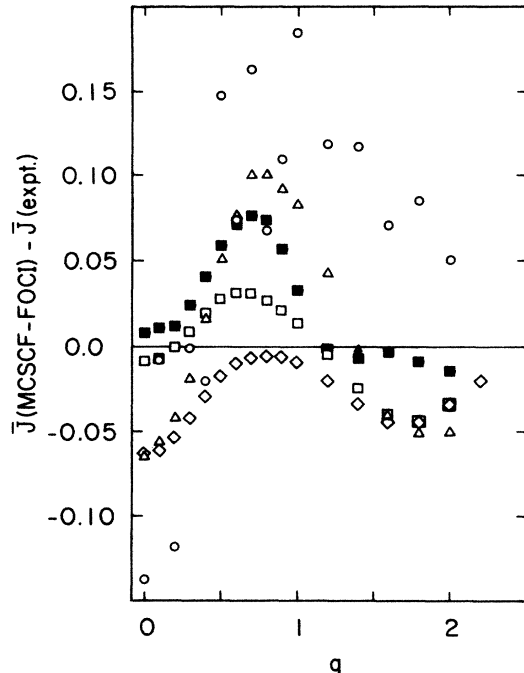


FIG. 1. Differences between the MCSCF-FOCI and experimental isotropic Compton profiles. Typical uncertainties in the profiles obtained from photon scattering experiments are 1% of  $\bar{J}(0)$  or  $\pm 0.05$ .  $\circ$ , 25 keV electron scattering at  $12^\circ$  (Ref. 15);  $\triangle$ , average (Ref. 12) of Ag  $K\alpha$  and Mo  $K\alpha$  x-ray scattering results (Ref. 11);  $\square$ , original results from  $173^\circ$  scattering of 160 keV  $\gamma$  rays (Ref. 12);  $\diamond$ , reanalyzed results (Ref. 13) from  $173^\circ$  scattering of 160 keV  $\gamma$ -rays;  $\blacksquare$ , results from scattering of 60 keV  $\gamma$  rays (Ref. 14).

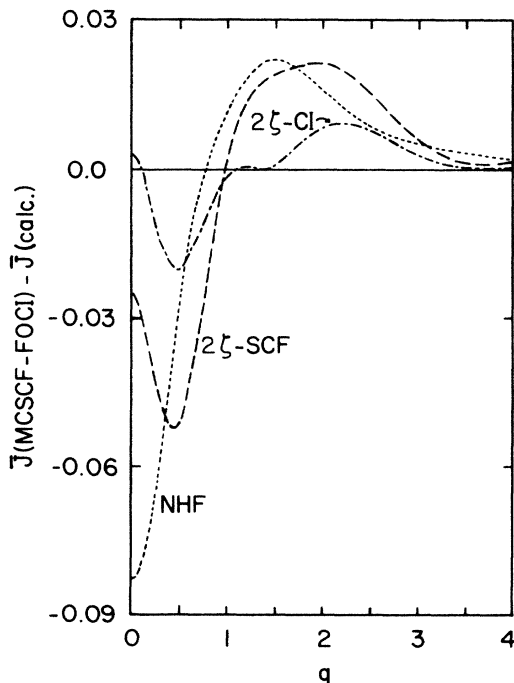


FIG. 2. Differences between the MCSCF-FOCI and other theoretical isotropic Compton profiles.  $\cdots$ , calculated (Ref. 25) from an NHF wave function (Ref. 35);  $---$ , calculated from a SCF wave function in a double  $\zeta$  basis of GLF's (Ref. 23);  $- \cdot - \cdot -$ , calculated from a CI wave function in a double  $\zeta$  basis of GLF's (Ref. 23).

which is more than twice as large as the deviation of  $\bar{J}_{2\zeta\text{-CI}}$  given in Table II. Note also that the rule of thumb<sup>42,55</sup> that  $\bar{J}(0)$  is lower for wave functions with lower energies is not always satisfied by the values in Table II.

### B. Small- $q$ behavior of the ICP

The quantities  $\Pi_0(0)$  and  $\Pi_0''(0)$  which appear in the MacLaurin expansion of the ICP have been estimated<sup>15</sup> from experimental electron-impact ICP's but not from photon scattering experiments. Hence values of these quantities were extracted from the photon scattering<sup>11-14</sup> data by local fits of the ICP's near  $q=0$  to polynomials in  $q^2$ . All these values are compared with values computed from the NHF wave function and the MCSCF-FOCI wave function as well as some previous theoretical estimates<sup>57</sup> in Table III.

All the experimental  $\Pi_0(0)$  values are slightly higher than the MCSCF-FOCI value although the latter lies within most of the experimental error bars. The MCSCF-FOCI value of  $\Pi_0''(0)$  is in good agreement with the experimental values. The theoretical values attributed to Langhoff<sup>57</sup> seem to be in error as does the conclusion<sup>15,57</sup> drawn from them that even rough experimental estimates of  $\Pi_0(0)$  and especially  $\Pi_0''(0)$  can provide very sensitive tests of electron correlation. The differences between the NHF and MCSCF-FOCI values are only 6.6% and 2.3%, respectively, for  $\Pi_0(0)$  and  $\Pi_0''(0)$ .

TABLE III. Comparison of theoretical and experimental values of the isotropic EMD and its second derivative at  $p=0$ .

	$\Pi_0(0)$	$\Pi_0''(0)$
Electron-impact expt. <sup>a</sup>	$1.66 \pm 0.19$	$-8.2 \pm 5.2$
Electron-impact expt. <sup>b</sup>	$1.56 \pm 0.31$	$-4 \pm 2$
X-ray expt. <sup>c</sup>	$1.51 \pm 0.20$	$-3.1 \pm 1.3$
160 keV $\gamma$ -ray expt. <sup>d</sup>	$1.39 \pm 0.04$	$-2.9 \pm 1.5$
160 keV $\gamma$ ray expt. <sup>e</sup>	$1.40 \pm 0.09$	$-2.8 \pm 1.0$
60 keV $\gamma$ -ray expt. <sup>f</sup>	$1.40 \pm 0.17$	$-2.7 \pm 1.4$
SCF calculation <sup>g</sup>	1.20	1.00
Hartree-Fock <sup>h</sup>	1.4079	-2.772
Hybrid CI estimate <sup>g</sup>	1.23	-1.80
MCSCF-FOCI <sup>i</sup>	1.3206	-2.839

<sup>a</sup>Reference 15. Obtained by a fit of the measured ( $12^\circ$ ) ICP near  $q=0$  to a polynomial in  $q^2$ .

<sup>b</sup>Reference 15. Obtained by a global fit of the measured ( $12^\circ$ ) ICP to a linear combination of Lorentzian functions.

<sup>c</sup>Present work. Obtained by fits of the small  $q$  ICP of Ref. 11 to a cubic polynomial in  $q^2$ .

<sup>d</sup>Present work. Obtained by fits of the small  $q$  ICP of Ref. 12 to a quartic polynomial in  $q^2$ .

<sup>e</sup>Present work. Obtained by fits of the small  $q$  ICP of Ref. 13 to a quartic polynomial in  $q^2$ .

<sup>f</sup>Present work. Obtained by fits of the small  $q$  ICP of Ref. 14 to a cubic polynomial in  $q^2$ .

<sup>g</sup>Reference 57.

<sup>h</sup>Present work. Computed from the NHF wave function of Ref. 36.

<sup>i</sup>Present work. Computed from the MCSCF-FOCI wave function.

TABLE IV. Moments of the electron momentum distribution.

Moment	Expt. <sup>a</sup>	NHF <sup>b</sup>	MCSCF-FOCI <sup>c</sup>
$\langle p^{-2} \rangle$	17.1±1.9	16.405	15.809
$\langle p^{-1} \rangle$	10.7±0.8	10.689	10.524
$\langle p^0 \rangle^d$	13.4±1.6	14.000	14.000
$\langle p \rangle$	36 ± 7	38.044	38.294
$\langle p^2 \rangle$	210 ± 71	217.58	218.60
$\langle p^3 \rangle$	$(2.3 \pm 1.1) \times 10^3$	$2.2650 \times 10^3$	$2.2682 \times 10^3$
$\langle p^4 \rangle$	$(5.0 \pm 2.8) \times 10^4$	$4.4962 \times 10^4$	$4.4897 \times 10^4$

<sup>a</sup>Reference 15.

<sup>b</sup>Present work. Computed from the NHF wave function of Ref. 36. See also Ref. 25.

<sup>c</sup>Present work. Computed from the MCSCF-FOCI wave function.

<sup>d</sup>Exactly equal to the number of electrons. The entries provide a check of the normalization.

### C. Moments of the EMD

Moments have not been reported<sup>10-14</sup> for the photon scattering EMD's, and no attempt has been made to obtain them in this work because the extraction of moments from experimental ICP's is a nontrivial task that is quite sensitive to the method used to perform the large- $q$  extrapolation.<sup>45</sup> The moments  $\langle p^k \rangle$  ( $-2 \leq k \leq 4$ ) of the EMD as estimated from an electron-impact experiment<sup>15</sup> are compared in Table IV with values computed from the NHF wave function and the MCSCF-FOCI wave function. The calculated values are all within the fairly large uncertainties of the experimental values. The accuracy of the experimental  $\langle p^3 \rangle$  and  $\langle p^4 \rangle$  values is surprising in view of the fact that the experimental ICP's extend to  $q=5$  only. This accuracy is probably due to the use of a Lorentzian fitting form together with a fortuitously accurate asymptotic constant.<sup>45</sup>

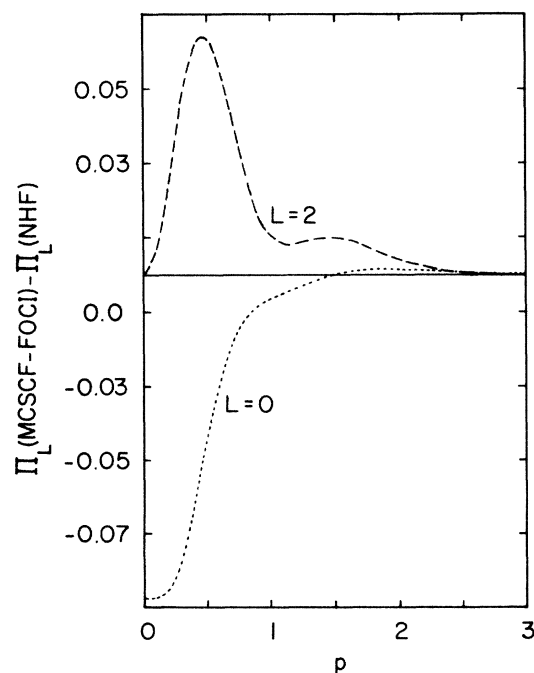


FIG. 3. Differences between the MCSCF-FOCI and NHF partial waves of the momentum density. · · · ·,  $L=0$ ; - - -,  $L=2$ .

Comparison of the NHF and MCSCF-FOCI moments shows, as expected,<sup>42,55</sup> that correlation results in a shift of probability density from low to high momentum. This is graphically illustrated in Fig. 3 which shows the difference between the correlated and NHF  $\Pi_0(p)$ . The correlation effects on  $\langle p^3 \rangle$  and  $\langle p^4 \rangle$  seem to be quite small with the latter being *lowered* by correlation; however, this may be a spurious result due to the absence of core correlation in the MCSCF-FOCI wave function. A more complete comparison of  $\langle p^{-1} \rangle = 2\bar{J}(0)$  values from various sources has already been made in Sec. III A.

### IV. ANISOTROPIC PROPERTIES

Directional Compton profiles, parallel and perpendicular to the molecular axis, computed from the MCSCF-FOCI wave function are listed in Table I. Inclusion of polarization functions in the basis set is essential if accurate bond-parallel DCP's are to be obtained.<sup>25</sup> Unlike the best previous CI calculation<sup>23</sup> of the DCP's of  $N_2$ , the  $(4s,4p,2d)$  STF basis set used in this work *does* contain polarization functions. However, even this basis set is unlikely to be large enough to ensure convergence of properties of the anisotropic EMD. Consider Table V which lists values of  $J(0, \gamma)$  computed from the SCF wave function in this basis set, the NHF wave function and the

TABLE V. Comparison of uncorrelated and correlated  $J(0, \gamma)$  surfaces.

$\gamma$ (deg.)	SCF <sup>a</sup>	NHF <sup>b</sup>	MCSCF-FOCI <sup>c</sup>
0	5.8499	5.9582	5.7452
15	5.6459	5.7365	5.5521
30	5.3395	5.4088	5.2681
45	5.2056	5.2599	5.1562
60	5.2301	5.2654	5.1962
75	5.3036	5.3213	5.2781
90	5.3385	5.3491	5.3156

<sup>a</sup>Present work. Computed from the SCF wave function built from the  $(4s,4p,2d)$  STF basis set.

<sup>b</sup>Present work. Computed from the NHF wave function of Ref. 36. See also Ref. 25.

<sup>c</sup>Present work. Computed from the MCSCF-FOCI wave function built from the  $(4s,4p,2d)$  STF basis set.

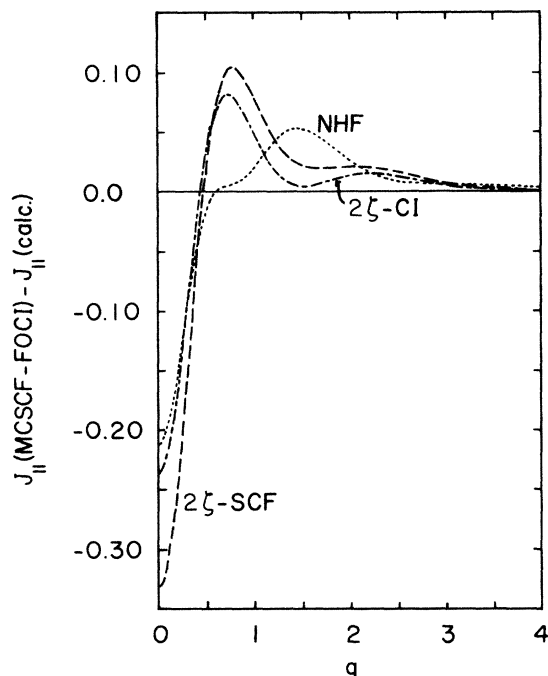


FIG. 4. Differences between the MCSCF-FOCI and other theoretical Compton profiles parallel to the molecular axis. Legend as in Fig. 2.

MCSCF-FOCI wave function. Evidently, the  $(4s,4p,2d)$  SCF values differ appreciably from the NHF limit for small angles. Recalling Shavitt's observation<sup>58</sup> that "no amount of configuration-interaction can remedy defects due to basis set inadequacies in the underlying SCF calculation," it is evident that the MCSCF-FOCI values of the

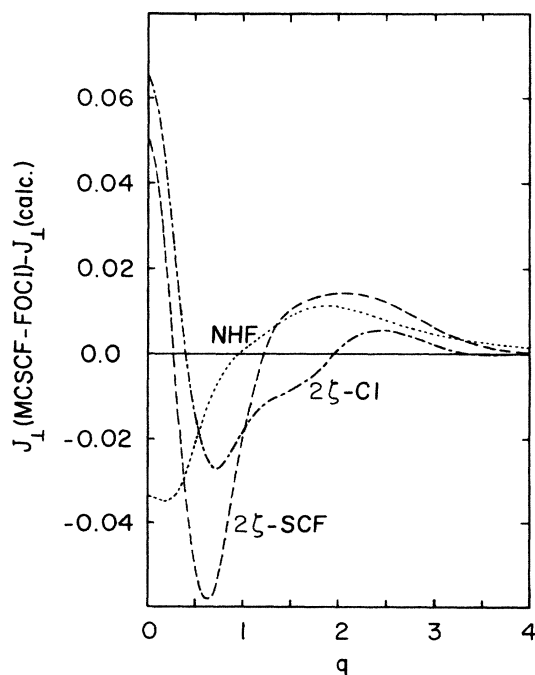


FIG. 5. Differences between the MCSCF-FOCI and other theoretical Compton profiles perpendicular to the molecular axis. Legend as in Fig. 2.

DCP's and other anisotropic properties cannot be considered definitive.

In view of these reservations about the basis set used and the fact that no experimental DCP's are available, the discussion of anisotropic properties will be restricted to a few tentative comments. Table V shows that the correlated values of  $J(0,\gamma)$  are consistently lower than the uncorrelated ones, and the differences decrease as  $\gamma$  increases from 0 to  $\pi/2$ . Figures 4 and 5 show that the MCSCF-FOCI DCP's are closer to the NHF ones than to the previous CI calculations<sup>23</sup> based on a double- $\zeta$  basis set of Gaussian lobes which is even more inadequate<sup>25</sup> than the  $(4s,4p,2d)$  STF set. Figure 3 shows that the correlated  $\Pi_2(p)$  is greater than the NHF one essentially everywhere. This suggests that correlation transfers momentum density from directions perpendicular to the bond to directions parallel to the bond. Such an effect has also been noted<sup>59</sup> for  $H_2$ . Finally, note that the  $(4s,4p,2d)$  SCF, NHF, and MCSCF-FOCI values of the kinetic energy anisotropy  $\Delta T$  are 0.1988, 0.0272, and 0.1621, respectively.

## V. CONCLUDING REMARKS

All the calculations reported here pertain to a bond length  $R$  of  $2.068a_0$  and not the more recent<sup>48(b)</sup> experimental value of  $2.074a_0$ . Moreover, molecular vibrations have not been taken into account. Fortunately, neither of these shortcomings is significant. An estimate of the vibrational effect can be obtained with the help of the  $\delta$  approximation<sup>60</sup>

$$\langle \phi_{vJ} | P(R) | \phi_{vJ} \rangle \simeq P(R_{vJ}) \quad (13a)$$

in which  $P(R)$  is an  $R$ -dependent property,

$$R_{vJ} = \langle \phi_{vJ} | R | \phi_{vJ} \rangle, \quad (13b)$$

and  $\phi_{vJ}$  is the nuclear motion wave function corresponding to the vibrational and rotational quantum numbers  $v$  and  $J$ , respectively. The latest spectroscopic constants<sup>48(b)</sup> together with Ogilvie and Tipping's formula<sup>61</sup> yield  $R_{00} = 2.081a_0$ . Thus, the average value of an  $R$ -dependent property of  $N_2$  in its ground vibrational and rotational state is approximately equal to its value at  $R = 2.081a_0$ . A previous NHF level study<sup>25</sup> of the effect of varying the internuclear separation on the momentum-space properties of  $N_2$  suggests that the values at  $R = 2.081a_0$  of  $\bar{J}(0)$  and  $\langle p^{-2} \rangle$  will be higher by 0.1% and those of  $\Pi_0(0)$  and  $\langle p \rangle$  will be lower by 0.07% and 0.06%, respectively, than their values at  $R = 2.068a_0$ . Shifts of half this size can be expected for momentum-space properties at  $R = 2.074a_0$ . These effects are smaller than the residual errors in our Compton profiles due to the impulse approximation. Very similar conclusions can be drawn from a Hartree-Fock-Slater level study<sup>29(b)</sup> of vibrational effects.

The isotropic Compton profile of  $N_2$  presented in this work is expected to be of a quality similar to that of cal-

culations available for neon,<sup>53</sup> water,<sup>62–65</sup> ammonia,<sup>62</sup> and methane,<sup>62,66</sup> but not quite as accurate as the benchmark calculations for helium<sup>67</sup> and molecular hydrogen.<sup>60,68</sup> Calculations with a larger basis set will be required to obtain converged values of anisotropic properties such as the bond-parallel DCP.

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