Momentum-space properties of N_2: Improved configuration-interaction calculations

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Properties that depend on the anisotropy of the electron momentum distribution of N_2 are not easy to calculate accurately. Even rather elaborate work [Phys. Rev. A **36**, 5111 (1987)] concluded that computations using still better one-particle basis sets were necessary. This paper reports improved configuration-interaction calculations that use a better basis set and also take explicit account of molecular vibration. Most of our results have converged to an accuracy of 0.5% or better. However, it turns out unexpectedly that the coefficients in the MacLaurin expansion of the isotropic Compton profile need to be verified by further theoretical and/or experimental work.

I. INTRODUCTION

Electron momentum distributions (EMD's) in atoms, molecules, and solids have been studied using many techniques including x-ray and γ-ray Compton scattering, positron annihilation, high-energy electron impact, binary $(e,2e)$ reactions, and quantum-mechanical calculations.[1-3] It is important that the EMD's of some simple systems be studied as thoroughly as possible in order to establish reference points against which newer theories and experiments can be tested. N_2 is one of the substances suitable for this purpose and hence a large number of studies, both theoretical and experimental, of the EMD of $^1\Sigma_g^+ N_2$ have been carried out.[4-6]

The most accurate γ-ray measurements of the isotropic Compton profile (ICP) of N_2 are in agreement with calculations based on configuration-interaction (CI) wave functions.[5,6] No experimental measurements have yet been made of properties, such as directional Compton profiles (DCP's), that depend on the *anisotropy* of the EMD of N_2. Hence our knowledge of anisotropic properties comes solely from theoretical calculations; although the DCP's of N_2 have been obtained to an accuracy of roughly 1% by the most sophisticated calculations to date,[6] fully converged values of quantities such as the kinetic-energy anisotropy are still unavailable.

Previous work[6] has clearly indicated that improving the one-particle basis set is the key to further improvement of the calculations. The purpose of this paper is to report calculations based on a series of CI wave functions using a basis set substantially better than those used in previous work. Moreover, unlike previous work, the effects of molecular vibration are explicitly calculated. Details of the wave functions are given in Sec. II. Properties of the isotropic EMD and properties that depend upon the anisotropy of the EMD are presented in Secs. III and IV, respectively. Hartree atomic units are used throughout this paper.

II. WAVE FUNCTIONS

A. One-particle basis set

The one-particle basis set of Slater-type functions (STF's), designed by Sekiya and Tatewaki[7] and denoted by T, consists of $(5s,5p,4d,3f)$ STF's on each atom. Its quality can be assessed by comparison of self-consistent-field (SCF) calculations in basis T with the Hartree-Fock (HF) limit results obtained by purely numerical methods.[8] Such a comparison is made in Table I which also includes results for two other basis sets of STF's. One of these is set L (Ref. 9) which was used in the previous best momentum-space calculations;[6] it consists of $(5s,3p,3d,1f)$ STF's for the σ molecular orbitals (MO's) and $(3p,2d,1f)$ STF's for the π MO's. Set L is simply the σ_g,π_u subset of basis set C (Ref. 10) which was considered, for many years, to be the best available one. Table I shows that set T yields an SCF energy which is $0.6mE_H$ above the HF limit[8] and is $0.4mE_H$ lower than those obtained from sets L and C.

Table I also contains a comparison of SCF multipole moments obtained from the various basis sets with the pertinent HF limit values.[8] Values of $\langle r^2\rangle = 2\langle x^2\rangle + \langle z^2\rangle$, a quantity that is related to the diamagnetic susceptibility, are also included. The first three nonvanishing multipole moments[11] for a homonuclear diatomic molecule A_2, with its high-symmetry axis along the z axis, are given by

$$Q_2 = Z_A R^2/2 - (\langle z^2\rangle - \langle x^2\rangle)\,, \tag{1}$$

$$Q_4 = Z_A R^4/8 - (\langle z^4\rangle + \langle x^4\rangle - 6\langle x^2 z^2\rangle)\,, \tag{2}$$

and

$$Q_6 = Z_A R^6/32 - [\langle z^6\rangle - \langle x^6\rangle + 15(\langle x^4 z^2\rangle - \langle x^2 z^4\rangle)] \tag{3}$$

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in which R is the bond length, Z_A is the atomic number of the constituent atoms, the origin is at the inversion center, and

$$\langle x^m z^n \rangle = \int \rho(x,y,z) x^m z^n dx\, dy\, dz \ , \quad (4)$$

where $\rho(x,y,z)$ is the one-electron charge density normalized to the number of electrons N. These properties emphasize the outer regions of position space and therefore serve as probes of the inner regions of momentum space.[1,12-15]

Basis set T has an energy and quadrupole moment Q_2 in substantially better agreement with the HF limit than the other sets. However, basis L has the Q_4 closest to the HF limit, and set C has the $\langle r^2 \rangle$ closest to the HF limit. Moreover, set T is not much better than set L for Q_6. It is not immediately evident which is the overall best basis set. Hence, some objective method must be used to choose among these basis sets. An information theory technique[16] was used to rank the basis sets with respect to each of the property sets $\{E, Q_2, Q_4, Q_6, \langle r^2 \rangle\}$, $\{Q_2, Q_4, Q_6\}$, and $\{Q_4, Q_6, \langle r^2 \rangle\}$. Note that the first set contains all five properties, the second set omits E and $\langle r^2 \rangle$ which are more "averaged" than the direction-sensitive multipole moments, and the third set omits the two properties for which basis set T is clearly the best. It turns out that basis set T is ranked best for *all three* property sets. We are particularly impressed by the ranking for the third property set which was deliberately biased against set T. We conclude that basis set T predicts results closest to the HF limit in an overall sense.

B. Correlated wave functions

Four different CI wave functions were constructed using $C_{\infty v}$ symmetry and the iterative natural orbital (INO) technique.[17] The STF basis set results in 34 symmetry-adapted basis functions (SAF's) of σ symmetry, 24 SAF's of π symmetry, 14 SAF's of δ symmetry, and 6 SAF's of ϕ symmetry. The first wave function, denoted T-CI1, employs only σ and π orbitals and is constructed by a prescription similar to that of a "first-order" wave function.[18] The INO iterations were begun with the SCF MO's. The orbitals were divided into three classes: (1) frozen (f) orbitals: $1\sigma, 2\sigma$, (2) valence (v) orbitals: $3-12\sigma$ and $1-6\pi$, (3) higher (h) orbitals: $13-34\sigma$ and $7-24\pi$. All configuration state functions (CSF's) which differed from the reference SCF function by one- and two-electron excitations from the v set were included in

TABLE I. Energies and position-space properties.

Method[a]	$-E$	E_C (%)[b]	E_{vc} (%)[c]	$-Q_2$	$-Q_4$	$-Q_6$	$\langle r^2 \rangle$
L-SCF	108.992 76	0	0	0.9718	7.179	15.2	39.061
C-SCF	108.9928	0	0	0.9472	6.843	13.1	39.019
T-SCF	108.993 20	0	0	0.9379	7.044	15.4	39.013
HF limit[d]	108.993 81	0	0	0.9400	7.392	16.9	39.032
L-CI2E	109.321 02	61	75	1.2009	6.736	13.3	38.978
T-CI1	109.274 931	52	65	1.1874	6.763	13.1	38.930
T-CI2	109.347 989	66	82	1.1165	6.432	12.2	38.830
T-CI3	109.349 175	66	82	1.1151	6.423	12.2	38.834
T-CI4	109.355 931	67	83	1.1397	6.423	12.2	38.832
T-CI4V[e]				1.1183	6.499	12.5	39.043
SD-CI[f]	109.4019	76	g	1.0645			38.870
MRSD-CI[h]	109.4268	80	g	1.0905			38.911
SDQ-MP4[i]	109.319 676	61	75	1.1131	6.76		
Expt.[j]				1.09±0.07			
Expt.[k]					8.0±2.4		

[a]All our wave functions are designated by a letter indicating the Slater basis (L, C, or T) and a symbol indicating the method used. See text for details.
[b]Percentage of empirical total correlation energy (-0.5382, Ref. 21) obtained relative to the HF limit.
[c]Percentage of empirical valence-shell correlation energy (-0.4337, Ref. 22) obtained relative to the HF limit.
[d]Fully numerical calculations (Ref. 8).
[e]Vibrationally averaged values. See text for details.
[f]CI calculations at $R = 2.0743a_0$ (Ref. 25).
[g]The calculations of Ref. 25 include core correlation so E_{vc} is undefined.
[h]Multireference singles-doubles CI calculations at $R = 2.0743a_0$ (Ref. 25).
[i]Fourth-order many-body perturbation theory results for $R = 2.07432a_0$ (Ref. 26). SDQ indicates that only contributions from single, double, and unlinked quadruple excitations are included.
[j]Induced optical birefringence (Ref. 23).
[k]Infrared collision-induced absorption (Ref. 24).

the CI expansions provided that no more than one electron was in an orbital in the h set. The fourth iterate is T-CI1 which contains 4781 CSF's.

Next, an intermediate calculation was carried out in a truncated one-particle basis set of 12σ, 6π, 14δ, and 6ϕ SAF's. The zeroth iteration used the natural orbitals (NO's) of T-CI1, and δ and ϕ SAF's. All single and double excitations not originating in the core (1σ and 2σ) were included in the CI expansion which contained 3039 CSF's. The δ and ϕ NO's produced in the third iteration together with the σ and π NO's of T-CI1 form the starting point for all subsequent calculations.

The T-CI2 wave function was constructed as follows. Calculations on atomic nitrogen using the STF basis were used as a guide to select the lowest 26 σ and 16 π NO's of T-CI1, and 8 δ and 2 ϕ NO's from the intermediate calculation. Frozen-core (FC), all single- and double-excitation (SD) CI calculations were carried out at each step of the INO iterations. The second iterate is T-CI2 which contains 7024 CSF's.

Next, a 5×10^{-6} occupation number threshold was used to select 23 σ and 17 π NO's from T-CI1, and 11 δ and 5 ϕ NO's from the intermediate calculation. T-CI3, which contains 7546 CSF's, is the second iterate from the subsequent INO-FC-SD-CI calculations using these NO's in the zeroth iteration.

T-CI4 used the same starting NO's as T-CI3 and a similar calculation method except that no restrictions were placed on the occupancies of the 3σ, 4σ, 5σ, 6σ, 1π, and 2π orbitals. This allows some multiple (up to six-fold) excitations into the CI expansion. The first iterate in these calculations is T-CI4 which contains 7695 CSF's.

All these wave functions were constructed with the ALCHEMY program system,[19] and correspond to the $^1\Sigma_g^+$ state at a bond length[20] of 2.068 a_0.

The accuracy of the wave functions is indicated by Table I which lists values of the energy E, $\langle r^2\rangle$, and the multipole moments Q_2, Q_4, and Q_6 corresponding to each of them. Values for L-CI2E, the previous best wave function used for momentum-space calculations,[6] semiempirical estimates,[21,22] experimental values[23,24] and other theoretical values[25,26] are also included. Table I shows that the T-CI1, T-CI2, T-CI3, and T-CI4 wave functions, respectively, recover 52%, 66%, 66%, and 67% of the estimated[21] total correlation energy. Obviously, these correspond to higher percentages (65%, 82%, 82%, and 83%, respectively) of the estimated[22] valence-shell correlation energy which is perhaps the more suitable reference since no allowance has been made for core electron correlation in any of these wave functions. T-CI2, T-CI3, and T-CI4 are energetically superior to L-CI2E and, unlike the latter, all yield quadrupole moments in agreement with experiment and the most recent theoretical values. The 2% difference between the Q_2 predicted by T-CI4, and those predicted by T-CI2 and T-CI3 indicates that the higher excitations included in T-CI4 are significant; this conclusion can also be inferred from the 2% difference, in the same direction, between the Q_2 values predicted by the SD-CI and multireference singles-doubles (MRSD)-CI wave functions of Feller *et al.*[25]

The discussion in Sec. II A showed that the one-particle basis set T is superior to set L. The above paragraph shows that the many-particle basis set, in other

TABLE II. Isotropic Compton profiles and their small-q behavior. Error bars for experimental $J_0(q)$ values are ±0.05. Values in parentheses are estimated uncertainties.

Method	$J_0(0)$	$J_0(0.5)$	$J_0(1.0)$	$J_0(2.0)$	$\Pi_0(0)$	$\Pi_0''(0)$
L-SCF	5.3491	4.3639	2.5444	0.7550	1.4075	−2.469
C-SCF	5.3443	4.3646	2.5475	0.7546	1.4079	−2.772
T-SCF	5.3495	4.3605	2.5487	0.7540	1.4485	−3.765
L-CI2E	5.3069	4.3204	2.5416	0.7746	1.4319	−3.013
T-CI1	5.3249	4.3142	2.5443	0.7720	1.5441	−5.692
T-CI2	5.3119	4.3114	2.5492	0.7729	1.5237	−5.506
T-CI3	5.3127	4.3112	2.5490	0.7730	1.5271	−5.570
T-CI4	5.3103	4.3087	2.5488	0.7741	1.5284	−5.600
T-CI4V	5.3155	4.3131	2.5484	0.7720	1.5277	−5.552
Expt.[a]	5.271	4.309	2.545	0.805	1.39(0.04)	−2.9(1.5)
Expt.[b]	5.325	4.354	2.568	0.805	1.40(0.09)	−2.8(1.0)
Expt.[c]	5.254	4.278	2.526	0.785	1.40(0.17)	−2.7(1.4)
Expt.[d]	5.327	4.286	2.476	0.821	1.51(0.20)	−3.1(1.3)
Expt.[e]	5.399	4.189	2.374	0.720	1.56(0.31)	−4.0(2.0)

[a]160-keV γ-ray measurements of Ref. 31.
[b]160-keV γ-ray measurements of Ref. 31 as reanalyzed in Ref. 32.
[c]60-keV γ-ray measurements of Ref. 33.
[d]Average of Ag $K\alpha$ and Mo $K\alpha$ x-ray measurements of Ref. 30 as listed in Ref. 31.
[e]25-keV electron-impact measurements of Ref. 34.

words the treatment of electron correlation, is more nearly complete in T-CI2, T-CI3, and T-CI4 than in L-CI2E. Thus, momentum-space properties predicted by the T-CI2, T-CI3, and T-CI4 wave functions should be considered more reliable than the previous best calculations[6] made with L-CI2E. It is difficult to be certain which of T-CI2, T-CI3, and T-CI4 will predict the most accurate momentum-space properties. Fortunately, the momentum-space predictions of these three wave functions are closer to one another than to those of L-CI2E. In the absence of any convincing evidence to the contrary, we assume that our energetically best wave function, T-CI4, is the most accurate of the three.

C. Vibrational effects

A vibrationally averaged estimate was obtained for each property $P(R)$ which depends on the bond length R by a Taylor series expansion truncated after the linear term:

$$\langle P(R)\rangle \simeq P(S)+\left[\frac{dP}{dR}\right]_S \langle R-S\rangle \ , \tag{5a}$$

where the angular brackets denote an average with respect to the ground vibration-rotation state and $S=2.068a_0$.

Then, a finite difference approximation to the derivative yields

$$\langle P(R)\rangle \simeq P(S)+[P(S_1)-P(S)]\langle R-S\rangle/(S_1-S) \ , \tag{5b}$$

where S_1 ($=2.058a_0$ in this work) is a bond length close to S. All calculations therefore had to be repeated at $R=S_1$. Experimental spectroscopic constants[27] and a well-known formula[28] were used to estimate $\langle R-S\rangle \simeq 0.013a_0$. The vibrationally averaged results are denoted T-CI4V. Use of the crude Eq. (5) is justified by the smallness of the vibrational effects.

III. ISOTROPIC PROPERTIES

A. Compton profiles

The isotropic Compton profile is given[1] in the impulse approximation by the DuMond relationship:

$$J_0(q)=2\pi\int_{|q|}^{\infty}\Pi_0(p)p\,dp \tag{6}$$

in which $\Pi_0(p)$ is the isotropic EMD. The calculation of the EMD from the natural orbitals was carried out in a standard manner.[29]

Table II contains both theoretical and experimental[30–35] values of the ICP at selected points. First, compare the various theoretical ICP's with one another. The differences among the various CI wave functions are very small ($<0.5\%$) and typically much smaller than the differences between the SCF and CI results. These results confirm our earlier demonstrations[5,6] that correlation beyond the first-order[18] level is unnecessary to obtain a reasonably well converged ICP. The effects of vibrational averaging are also very small as predicted earlier.[5,6,36,37]

Next, consider Table III which lists the rms deviations between each pair of experimental and theoretical ICP's. The CI results provide better agreement with three of the experimental data sets than their SCF counterparts do. The other two experimental data sets are in equally good agreement with the SCF and CI results. As noted earlier,[5] the x-ray and particularly the electron impact data are in worse agreement with the calculations than any of the γ-ray experiments. Bear in mind that the estimated uncertainty in the x- and γ-ray ICP's is 1% of $J_0(0)$ or 0.05. Since none of the CI calculations has an rms deviation greater than 0.042 with respect to any of the four photon scattering ICP's, these experiments cannot decide

TABLE III. rms deviations between experimental and calculated isotropic Compton profiles. Only points up to $q=5$ are included.

Method	160-keV γ ray[a]	160-keV γ ray[b]	60-keV γ ray[c]	X ray[d]	25-keV electrons[e]
L-SCF	0.048	0.031	0.060	0.059	0.089
T-SCF	0.047	0.030	0.059	0.060	0.089
L-CI2E	0.022	0.028	0.032	0.041	0.085
T-CI1	0.026	0.029	0.035	0.040	0.083
T-CI2	0.021	0.029	0.032	0.042	0.086
T-CI3	0.021	0.029	0.032	0.042	0.086
T-CI4	0.020	0.030	0.030	0.041	0.086
T-CI4V	0.023	0.029	0.033	0.042	0.085

[a]160-keV γ-ray measurements of Ref. 31.
[b]160-keV γ-ray measurements of Ref. 31 as reanalyzed in Ref. 32.
[c]60-keV γ-ray measurements of Ref. 33.
[d]Average of Ag $K\alpha$ and Mo $K\alpha$ x-ray measurements of Ref. 30 as listed in Ref. 31.
[e]25-keV electron-impact measurements of Ref. 34.

which of the CI profiles is the most accurate. Instead, as noted previously,[5,6] the theoretical results suggest that the original 160-keV γ-ray ICP reported by Eisenberger and Reed[31] is the most accurate measured profile; note, however, that the differences among the rms deviations are not sufficiently large to establish this unequivocally. Mendelsohn and Smith[38] found that the original[31] 160-keV γ-ray ICP for krypton was in closer agreement with the best calculation than the ICP obtained by reanalysis[32] of the data. Hence another reanalysis of the γray data[31] using the new and more accurate procedure of Ribberfors[39] would be interesting.

B. Small-q behavior of the ICP

Since experimental measurements of the ICP are most accurate near the peak, the leading coefficients of its MacLaurin expansion

$$J_0(q)=J_0(0)-\pi\Pi_0(0)q^2-[\pi\Pi_0''(0)/4]q^4\cdots \quad (7)$$

are of interest as well. Table II shows large basis set effects on $\Pi_0(0)$ and particularly $\Pi_0''(0)$; these effects are quite distressing in view of the fact that bases L, C, and T are all rather large. In view of the discussion in the last two paragraphs of Sec. II B, we assume that the T-CI2, T-CI3, and T-CI4 values are more accurate than the L-CI2E results. Table II shows that all four T-CI values of $\Pi_0(0)$ lie outside the error bars of the 160-keV γ-ray values,[31,32] although all CI values are in agreement with the x-ray, 60-keV γ-ray, and 25-keV electron impact results. Further work, both experimental and theoretical, is needed to clear up this discrepancy. Four of the experimental values of $\Pi_0''(0)$ disagree with the T-CI values. This is less disturbing since numerical second derivatives extracted from experimental data cannot be expected to be very reliable.

C. Moments of the EMD

Moments of the EMD are defined by

$$\langle p^k\rangle=4\pi\int_0^\infty \Pi_0(p)p^{k+2}dp, \quad -3<k<5\ , \quad (8)$$

where the limits on k arise from the p^{-8} asymptotic behavior[15] of $\Pi_0(p)$ and the fact that Π_0 is finite and

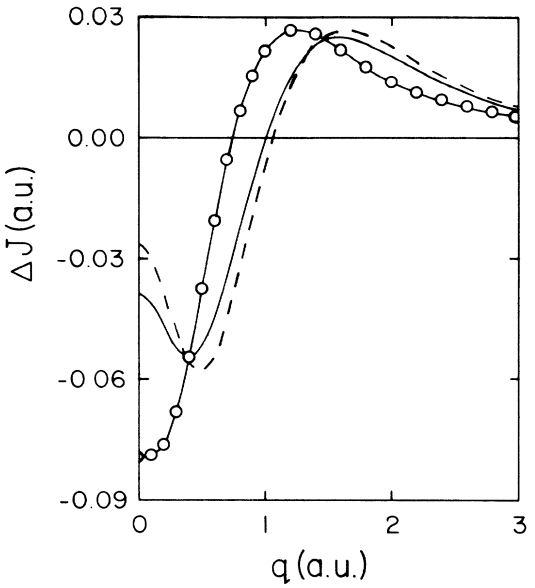

FIG. 1. Effects of electron correlation on the Compton profiles of N_2; differences between the T-CI4 and T-SCF values are shown. ——, ICP; — — —, perpendicular DCP; ○, parallel DCP.

nonzero at $p=0$. $\langle p\rangle$ is proportional to the Dirac-Slater exchange energy to a high degree of accuracy,[14] and $\langle p^3\rangle$ is roughly proportional[14] to the initial value of the Patterson function of x-ray crystallography. $\langle p^{-1}\rangle=2J_0(0)$ has already been considered in Sec. III A. Instead of $\langle p^2\rangle$ and $\langle p^4\rangle$, we list the nonrelativistic kinetic energy given by

$$T_{\rm NR}=\langle p^2\rangle/2 \quad (9)$$

and the Breit-Pauli correction[40] to it arising from the variation of electron mass with velocity:

$$H_{\rm MV}=-\alpha^2\langle p^4\rangle/8\ , \quad (10)$$

where α is the fine-structure constant. We also consider the full relativistic correction[41] to the nonrelativistic kinetic energy given by

TABLE IV. Properties of the isotropic momentum density.

Method	$\langle p^{-2}\rangle$	$\langle p\rangle$	$\langle p^3\rangle$	$T_{\rm NR}$	$H_{\rm MV}$	$H_{\rm RC}$
L-SCF	16.441	38.042	2264.9	108.788	−0.299 24	−0.268 32
C-SCF	16.405	38.044	2265.0	108.791	−0.299 29	−0.268 35
T-SCF	16.516	38.045	2264.9	108.793	−0.299 22	−0.268 31
L-CI2E	16.361	38.294	2269.8	109.366	−0.299 39	−0.268 47
T-CI1	16.677	38.283	2270.5	109.373	−0.299 48	−0.268 56
T-CI2	16.564	38.303	2270.7	109.400	−0.299 50	−0.268 58
T-CI3	16.575	38.303	2270.7	109.400	−0.299 50	−0.268 57
T-CI4	16.571	38.317	2270.9	109.430	−0.299 50	−0.268 58
T-CI4V	16.589	38.295	2270.7	109.390	−0.299 50	−0.268 58

TABLE V. Anisotropic properties of the electron momentum density.

Method	$J(0,0)$	$J(0,\pi/2)$	$J_2(0)$	$J_4(0)$	$J_6(0)$	ΔT	$\Pi_2(0.5)$
L-SCF	5.9583	5.3536	0.1652	0.2964	0.0976	0.0264	−0.1439
C-SCF	5.9582	5.3491	0.1663	0.2990	0.0981	0.0272	−0.1570
T-SCF	5.9532	5.3513	0.1659	0.2898	0.0979	0.0264	−0.1552
L-CI2E	5.8448	5.3306	0.1163	0.2797	0.0937	−0.0043	−0.1171
T-CI1	5.8967	5.3367	0.1407	0.2823	0.0979	−0.0309	−0.1382
T-CI2	5.8837	5.3252	0.1390	0.2843	0.0980	−0.0297	−0.1371
T-CI3	5.8843	5.3260	0.1388	0.2843	0.0980	−0.0304	−0.1371
T-CI4	5.8739	5.3248	0.1348	0.2815	0.0972	−0.0303	−0.1355
T-CI4V	5.8882	5.3285	0.1393	0.2840	0.0986	−0.0371	−0.1386

$$H_{\mathrm{RC}}=4\pi\alpha^{-2}\int_0^{\infty}[(1+\alpha^2p^2)^{1/2}-1-\alpha^2p^2/2]\Pi_0(p)p^2dp \ . \tag{11}$$

Extraction of the moments from an experimental ICP is a nontrivial task that is quite sensitive to the method used to perform the large-q extrapolation.[42] Hence, we have made no attempt to extract them from the photon scattering[30–33] ICP's. The moments obtained from electron-impact experiments[34] have rather large uncertainties and cannot[5,6] even distinguish SCF from CI results.

Thus only theoretical moments are listed in Table IV. Since core correlation is not included in any of the wave functions, and $\langle p^3\rangle$ and especially H_{MV} and H_{RC} are determined primarily by the core electrons,[41] only small basis set effects can be detected in Table IV for these quantities. Like $\Pi_0(0)$ and $\Pi_0''(0)$, $\langle p^{-2}\rangle$ is rather sensitive to basis set effects because it emphasizes small momenta and hence[1,12–15] the outer regions of the position space natural orbitals.

TABLE VI. T-CI4 and T-CI4V Compton profiles.

	$J_0(q)$		$J(q,0)$		$J(q,\pi/2)$	
q	T-CI4	T-CI4V	T-CI4	T-CI4V	T-CI4	T-CI4V
0.0	5.3103	5.3155	5.8739	5.8882	5.3248	5.3285
0.1	5.2627	5.2680	5.7782	5.7916	5.2797	5.2834
0.2	5.1248	5.1301	5.5127	5.5235	5.1467	5.1507
0.3	4.9091	4.9143	5.1291	5.1366	4.9335	4.9377
0.4	4.6315	4.6364	4.6851	4.6894	4.6526	4.6568
0.5	4.3087	4.3131	4.2263	4.2279	4.3207	4.3245
0.6	3.9571	3.9607	3.7815	3.7814	3.9566	3.9597
0.7	3.5923	3.5949	3.3670	3.3660	3.5790	3.5812
0.8	3.2285	3.2301	2.9900	2.9887	3.2048	3.2060
0.9	2.8777	2.8782	2.6525	2.6512	2.8472	2.8474
1.0	2.5488	2.5484	2.3533	2.3522	2.5154	2.5148
1.2	1.9769	1.9750	1.8576	1.8566	1.9478	1.9461
1.4	1.5288	1.5262	1.4765	1.4750	1.5112	1.5091
1.6	1.1936	1.1908	1.1860	1.1840	1.1884	1.1863
1.8	0.9497	0.9471	0.9661	0.9637	0.9540	0.9521
2.0	0.7741	0.7720	0.7994	0.7967	0.7839	0.7823
2.2	0.6472	0.6455	0.6714	0.6686	0.6590	0.6578
2.4	0.5539	0.5526	0.5712	0.5686	0.5654	0.5645
2.6	0.4833	0.4824	0.4915	0.4892	0.4933	0.4926
2.8	0.4281	0.4275	0.4274	0.4255	0.4360	0.4355
3.0	0.3833	0.3829	0.3758	0.3744	0.3890	0.3887
3.5	0.2988	0.2987	0.2865	0.2864	0.3004	0.3002
4.0	0.2365	0.2365	0.2317	0.2323	0.2360	0.2359
4.5	0.1875	0.1875	0.1909	0.1914	0.1865	0.1865
5.0	0.1484	0.1484	0.1545	0.1546	0.1476	0.1476

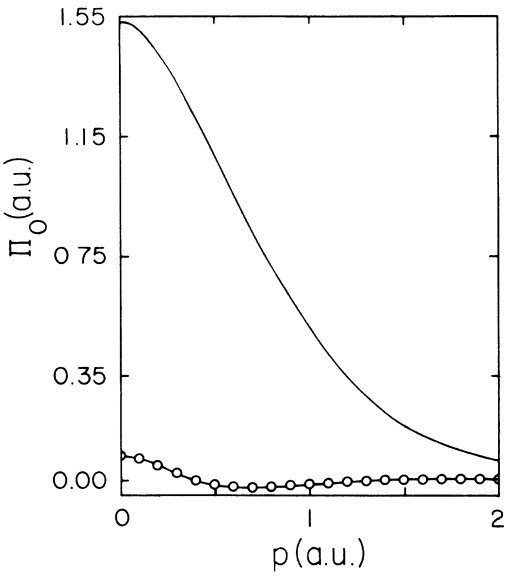

FIG. 2. First partial wave of the EMD of N_2(T-CI4). The difference between the T-CI4 and T-SCF values is shown with ○.

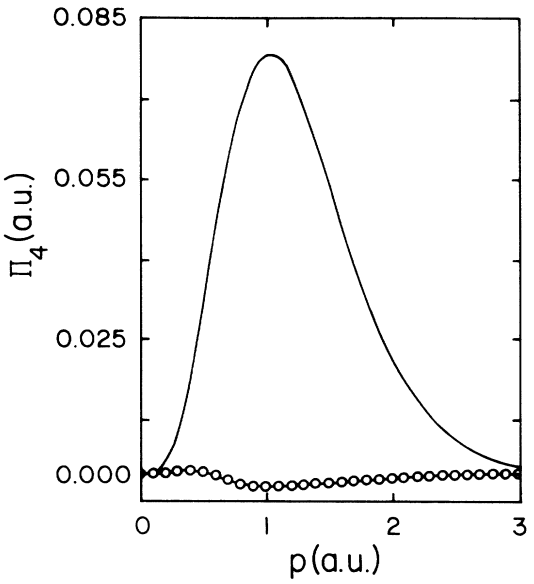

FIG. 4. Third partial wave of the EMD of N_2(T-CI4). The difference between the T-CI4 and T-SCF values is shown with ○.

IV. ANISOTROPIC PROPERTIES

The directional Compton profile is given[29] by

$$J(q,\mathbf{q}/q)=\int \Pi(\mathbf{p})\delta(\mathbf{p}\cdot\mathbf{q}/q-q)d\mathbf{p} \tag{12}$$

in which $\Pi(\mathbf{p})$ is the three-dimensional EMD and δ is the Dirac delta function. In a linear molecule, the EMD and DCP are independent of the azimuthal angle, and

$$\Pi(\mathbf{p})=\Pi(p,\theta) \tag{13}$$

and

$$J(q,\mathbf{q}/q)=J(q,\gamma) \tag{14}$$

in which θ and γ are the polar angles corresponding to $\mathbf{p}$ and $\mathbf{q}$, respectively. The anisotropy of the EMD and DCP is most conveniently studied with the help of partial-wave decompositions.[43,44] Thus,

$$\Pi(p,\theta)=\Pi_0(p)+\Pi_2(p)P_2(\cos\theta)+\Pi_4(p)P_4(\cos\theta)+\cdots \tag{15}$$

and

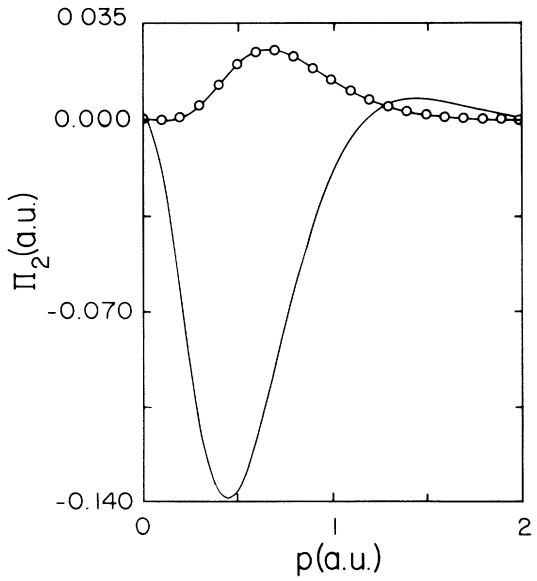

FIG. 3. Second partial wave of the EMD of N_2(T-CI4). The difference between the T-CI4 and T-SCF values is shown with ○.

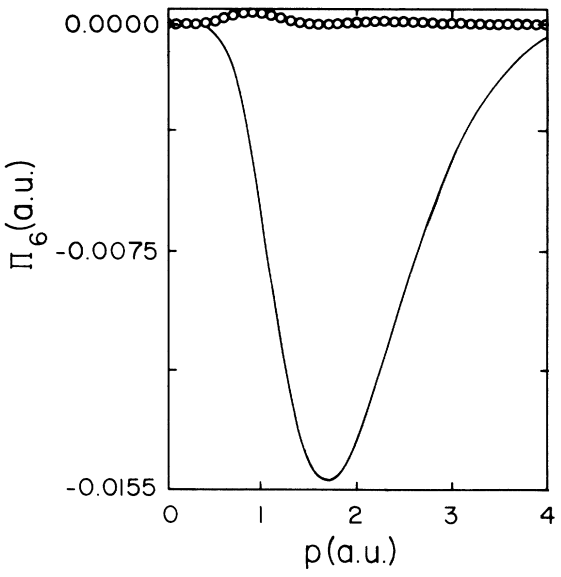

FIG. 5. Fourth partial wave of the EMD of N_2(T-CI4). The difference between the T-CI4 and T-SCF values is shown with ○.

$$J(q,\gamma)=J_0(q)+J_2(q)P_2(\cos\gamma)+J_4(q)P_4(\cos\gamma)+\cdots \tag{16}$$

where the P_L are Legendre polynomials. The leading terms of expansions (15) and (16) are the isotropic EMD and ICP, respectively, and the partial waves of J are related to those of Π by[43]

$$J_L(q)=2\pi\int_{|q|}^{\infty}\Pi_L(p)P_L(q/p)p\,dp\ . \tag{17}$$

Note that the DuMond relation, Eq. (6), is the $L=0$ case of Eq. (17). A quantity of great chemical interest[45] is the anisotropy of the kinetic energy tensor given by

$$\Delta T=\langle p^2P_2(\cos\theta)\rangle/2 \tag{18a}$$

$$=(2\pi/5)\int_0^{\infty}\Pi_2(p)p^4dp\ . \tag{18b}$$

Table V lists peak values of the DCP's parallel and perpendicular to the molecular axis calculated directly from Equation (12) as in Ref. 36, values of the partial waves J_L at $q=0$, ΔT, and the value of Π_2 at $p=0.5$ which is roughly the momentum at which Π_2 is largest in magnitude. There are non-negligible differences between the L-CI2E and T-CI4 values for many of these properties demonstrating how very sensitive they are to the quality of the wave function. The sign of ΔT which had been uncertain[6] now seems likely to be negative, contrary to early work.[5] Vibrational effects are small in comparison with correlation effects but of the same order of magnitude as the differences among the T-CI2, T-CI3, and T-CI4 values.

Figure 1 shows how electron correlation affects Compton profiles. Note that the effects are greatest on the parallel profile, and that the effects on the isotropic and perpendicular profiles are almost the same. Table VI lists our recommended ICP and DCP's; these values supersede our previous results.[5,6] Table VI shows that the effects of molecular vibration do not exceed 0.02 for the parallel DCP, and are smaller still for the ICP and the perpendicular DCP.

Figures 2–5 display the first four partial waves of the anisotropic EMD of the T-CI4 wave function. Their qualitative behavior is in accord with earlier work.[44] The effects of electron correlation are greatest for Π_2 which is reduced in magnitude at small p. Table VII lists these partial waves; the anisotropic EMD for small p may be reconstructed quite reliably from them because the convergence of the partial-wave expansion (15) is rather fast.[44] The effects of molecular vibration are most noticeable at small p.

TABLE VII. Partial waves of the T-CI4 and T-CI4V momentum densities.

	$\Pi_0(p)$		$\Pi_2(p)$		$\Pi_4(p)$		$\Pi_6(p)$	
p	T-CI4	T-CI4V	T-CI4	T-CI4V	T-CI4	T-CI4V	T-CI4	T-CI4V
0.0	1.5284	1.5277	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	1.5012	1.5007	−0.0202	−0.0206	0.0001	0.0001	−0.0000	−0.0000
0.2	1.4271	1.4272	−0.0672	−0.0685	0.0019	0.0019	−0.0000	−0.0000
0.3	1.3233	1.3242	−0.1130	−0.1153	0.0076	0.0078	−0.0000	−0.0000
0.4	1.2053	1.2070	−0.1369	−0.1398	0.0180	0.0184	−0.0001	−0.0001
0.5	1.0819	1.0840	−0.1355	−0.1386	0.0315	0.0323	−0.0003	−0.0003
0.6	0.9569	0.9593	−0.1165	−0.1192	0.0459	0.0470	−0.0008	−0.0008
0.7	0.8333	0.8356	−0.0896	−0.0917	0.0590	0.0603	−0.0016	−0.0017
0.8	0.7143	0.7164	−0.0624	−0.0638	0.0691	0.0707	−0.0028	−0.0029
0.9	0.6032	0.6049	−0.0387	−0.0396	0.0756	0.0772	−0.0044	−0.0046
1.0	0.5026	0.5040	−0.0203	−0.0207	0.0782	0.0797	−0.0063	−0.0065
1.1	0.4141	0.4152	−0.0073	−0.0075	0.0773	0.0786	−0.0083	−0.0086
1.2	0.3381	0.3388	0.0009	0.0009	0.0735	0.0746	−0.0103	−0.0106
1.3	0.2740	0.2744	0.0052	0.0053	0.0677	0.0686	−0.0120	−0.0124
1.4	0.2208	0.2211	0.0069	0.0069	0.0606	0.0613	−0.0134	−0.0138
1.5	0.1773	0.1774	0.0067	0.0067	0.0531	0.0535	−0.0144	−0.0148
1.6	0.1420	0.1420	0.0056	0.0055	0.0456	0.0459	−0.0150	−0.0154
1.7	0.1137	0.1136	0.0040	0.0039	0.0385	0.0387	−0.0152	−0.0156
1.8	0.0911	0.0910	0.0024	0.0022	0.0321	0.0322	−0.0150	−0.0154
1.9	0.0732	0.0730	0.0010	0.0008	0.0264	0.0264	−0.0146	−0.0149
2.0	0.0590	0.0588	−0.0002	−0.0004	0.0215	0.0215	−0.0139	−0.0142
2.2	0.0391	0.0389	−0.0016	−0.0018	0.0138	0.0137	−0.0121	−0.0123
2.4	0.0267	0.0265	−0.0021	−0.0023	0.0085	0.0084	−0.0101	−0.0102
2.6	0.0189	0.0188	−0.0021	−0.0023	0.0050	0.0049	−0.0080	−0.0081
2.8	0.0140	0.0140	−0.0018	−0.0019	0.0027	0.0026	−0.0062	−0.0062
3.0	0.0108	0.0108	−0.0015	−0.0015	0.0013	0.0013	−0.0046	−0.0045
3.5	0.0065	0.0065	−0.0007	−0..0007	0.0001	0.0001	−0.0017	−0.0017
4.0	0.0044	0.0044	−0.0002	−0.0002	0.0000	0.0001	−0.0004	−0.0003

V. CONCLUDING REMARKS

The work reported in this paper and the previous two[5,6] constitutes a major, but only partly successful, effort to calculate benchmark values of momentum-space properties of the dinitrogen molecule. Theoretical values which have converged to better than 0.5%, with respect to the one-particle basis set and *valence* correlation, have been obtained for the isotropic, bond parallel, and bond perpendicular Compton profiles, and the momentum moments. The $L > 0$ partial waves of the electron momentum density and directional Compton profile are not as well converged, and the best values of $J_L(0)$, ΔT, and $\Pi_2(0.5)$ in Table V are probably accurate to no better than 1%. Vibrational effects were found to be small in comparison with the effects of electron correlation but comparable to, or larger than, the differences among the results obtained from the three best wave functions.

There is a discrepancy between the electron impact ICP and all the theoretical and other experimental ICP's. The residual discrepancies between the γ-ray and theoretical correlated ICP are within the experimental uncertainties but, as suggested by Fig. 1 of the first paper in this series,[5] there may be a systematic error in the γ-ray data. There are significant discrepancies between the experimental and theoretical MacLaurin expansion coefficients of the ICP. These discrepancies suggest at least three courses of further inquiry. A purely numerical Hartree-Fock calculation of the kinetic energy anisotropy and the MacLaurin expansion coefficients of the ICP would be helpful in clarifying whether or not basis T is adequate for these properties. Fresh high accuracy experimental determinations of the ICP and especially its small-q behavior would be useful, and a reanalysis of the γ-ray data using the Ribberfors procedure may be helpful.

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