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Momentum-space properties of N_2

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Properties that depend on the anisotropy of the electron momentum distribution of $N_2(X\ ^1\Sigma_g^+)$ have not been determined accurately even by a fairly sophisticated calculation [Phys. Rev. A **34**, 4695 (1986)] using a configuration-interaction wave function. This paper reports calculations based on a series of wave functions designed to assess the sensitivity of one-electron momentum-space properties of N_2 to variations in the treatment of electron correlation and the choice of basis sets of Slater-type functions. The most elaborate of these wave functions, which consists of 169 650 configurations, provides satisfactorily converged predictions of a wide variety of isotropic momentum-space properties as well as *directional* Compton profiles. However, the anisotropy of the kinetic energy tensor turns out to be so small in magnitude that even its sign remains uncertain.

I. INTRODUCTION

Electron momentum distributions (EMD's) in atoms, molecules, and solids have been studied by 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]

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] However, properties that depend on the *anisotropy* of the EMD of N_2 are not yet known accurately. No experiments have been done so far, and even the most sophisticated calculations to date[5] have not produced fully converged values of quantities such as directional Compton profiles (DCP's) and the kinetic energy anisotropy.

The purpose of this paper is to report calculations based on a series of wave functions[6,7] designed to assess the sensitivity of one-electron properties of N_2 to variations in the treatment of electron correlation and the choice of basis set. The most elaborate of these wave functions yields converged results for most but not all anisotropic properties of interest. 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

Two different one-particle basis sets of atom-centered Slater-type functions (STF's) were considered. The first one, designed by Rumble *et al.*[6] and hereafter referred to as R, consists of $(4s,4p,2d)$ STF's composed from the $(4s,3p)$ "nominal" substrate of Bagus *et al.*[8] augmented by two $3d$ polarization STF's and a diffuse $2p$ STF. The second one, used by Liu *et al.*[7] and hereafter referred to as L, 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 and is simply the σ_g,π_u part of the basis set (hereafter referred to as C) constructed by Cade *et al.*,[9] who used a different basis set for the σ_u and π_g MO's.

Three different multireference CI wave functions in each of the R and L basis sets were considered. The reference function for the first two types (CI1 and CI2) contains 18 configuration state functions (CSF's) and was obtained by a complete-active-space (CAS) multiconfiguration (MC) self-consistent-field (SCF) procedure using the $3\sigma_g$, $1\pi_u$, $1\pi_g$, and $3\sigma_u$ MO's as the active space. CI1 and CI2, respectively, correspond to first- and second-order[10] CI relative to the 18-configuration CAS-MCSCF reference. The third wavefunction type (CI2E) corresponds to an approximate[7] second-order[10] CI with respect to a 96-configuration CAS-MCSCF reference obtained by enlarging the active space to include the $2\sigma_g$ and $2\sigma_u$ MO's. The CI2E wave functions contain 169 650 CSF's. All these wave functions were constructed with the ALCHEMY program system.[11] Further details can be found in Ref. 7.

Since each of these three types of wave function was constructed from two different basis sets, there is a total of six different CI wave functions designated by a letter indicating the basis set followed by the symbols defining the type of CI. All the wave functions correspond to the $X\,^1\Sigma_g^+$ state at a bond length[12] of $R=2.068a_0$. The R-CI1 wave function is identical to the MCSCF first-order CI wave function used previously for calculations of momentum-space properties[5] as well as high-energy electron scattering cross sections.[13] The L-CI1, L-CI2, L-CI2E, R-CI2, and R-CI2E wave functions were first used in a study of elastic electron scattering[7] in which they were designated CI1, CI2, CI3, CI4, and CI5, respectively.

In order to present an indication of the accuracy of these wave functions, Table I lists values[7,14] of the energy E, the quadrupole moment Q_2, and hexadecapole moment Q_4 corresponding to each of them. First consider the SCF results which can be judged against the Hartree-Fock (HF) limit attained by seminumerical partial-wave[15] and fully numerical[16] methods. The L and C basis sets give identical energies about $0.001E_h$ above the HF limit. The L and C basis sets respectively predict Q_2 values 3% and 1% different from the HF limit, and Q_4 values 3% and 7% different from the HF limit. Thus, both the L and C basis sets are fairly close to the HF limit. On the other hand, the R basis set has an energy $0.013E_h$ above the HF limit and, more significantly, Q_2 and Q_4 values which deviate by 25% and 15%, respectively, from the HF limit. This suggests that the R basis set is not adequate for describing one-electron properties that emphasize large electron-nucleus distances and, by inference,[1,17-20] small electron momenta. This difficulty with multipole moments confirms our earlier momentum-space study[5] which concluded that a basis set larger than set R would be necessary to obtain converged values of directional Compton profiles especially near their peak which depends heavily on the small momentum p behavior of the EMD.

Now consider the CI results of Table I. Table I shows that the L-CI1, L-CI2, and L-CI2E wave functions, respectively, recover 27%, 38%, and 61% of the estimated[21] total correlation energy. Obviously, these correspond to higher percentages (33, 47, and 75%, 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 the wave functions of Table I. At each of the three CI levels, the correlation energy recovered in the R basis set is a few percent less than that obtained in the larger L basis set. The most widely cited experimental value of the quadrupole moment is $(-1.09\pm0.07)ea_0^2$ obtained from induced optical birefringence measurements,[23] and the value obtained by a fourth-order many-body perturbation theory (MBPT) calculation[24,25]

TABLE I. Properties of the wave functions.

Wave function[a]	$-E$	$E_c\,\%$[b]	$E_{vc}\,\%$[c]	$-Q_2$	$-Q_4$
R-SCF	108.980 93	0	0	0.70	6.26
L-SCF	108.992 76	0	0	0.97	7.18
C-SCF	108.992 8	0	0	0.95	6.84
HF limit[d]	108.993 81	0	0	0.94	7.39
R-CI1	109.127 26	25	31	1.04	6.04
R-CI2	109.176 72	34	42	1.04	6.11
R-CI2E	109.291 75	55	69	0.98	5.62
L-CI1	109.137 29	27	33	1.25	7.05
L-CI2	109.196 93	38	47	1.26	7.15
L-CI2E	109.321 02	61	75	1.20	6.74
MBPT(4)[e]	109.385 81	73	90	1.15	

[a] All our wave functions are designated by a letter indicating the Slater basis (R, L, or C) 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. 16) which are in good agreement with seminumerical calculations (Ref. 15).

[e] Fourth-order many-body perturbation-theory calculations in a large Gaussian basis (Ref. 24).

is $-1.15ea_0^2$. The R basis set (which has a Q_2 much too small in magnitude at the SCF level) fortuitously gives a reasonable value at the CI1 and CI2 levels but a poor value at the CI2E level. On the other hand, the L basis set (which has a SCF Q_2 in good agreement with the HF limit[15,16]) predicts a Q_2 too large in magnitude at the CI1 and CI2 levels, but the value improves at the CI2E level. The experimental value[26] of the hexadecapole moment $[(-8.0\pm2.4)ea_0^4]$ is too uncertain to be of much guidance.

There is no guarantee that the energetically best wave function in this study (L-CI2E) is the most accurate for momentum-space properties. However, in view of the above discussion, we expect it to be.

III. ISOTROPIC PROPERTIES

A. Compton profiles

The isotropic Compton profile (ICP) is given[1] in the impulse approximation by the DuMond relationship,

$$J_0(q)=2\pi\int_{|q|}^{\infty}\Pi_0(p)p\,dp\ , \tag{1}$$

in which $\Pi_0(p)$ is the isotropic EMD. The calculation of the EMD from the natural orbitals (NO's) was carried out in a standard manner.[27]

Table II contains both theoretical and experimental[28–33] values of the ICP at selected points. First compare the various theoretical ICP values with one another. At any given level of wave-function approximation (SCF, CI1, CI2, or CI2E), there are significant differences between the values obtained from the R and L basis sets. On the basis of earlier work,[5] the discussion in Sec. II, and comparison of the R- and L-SCF results with the C-SCF values (Table II) obtained[5,34,35] from an SCF wave function[9] in the even larger C basis set, there seems little doubt that the results from the L basis set are superior to those from the R basis set. Next, note that for a given basis set (R or L), the differences among the three CI wave functions are much smaller than the differences between the SCF and CI1 results. It is clear that correlation beyond the CI1 (i.e., first-order[10]) level is unnecessary to obtain a reasonably well-converged ICP, thus vindicating our earlier supposition[5] that this was so. The same conclusion was first reached by Brown and Smith[36] from their careful study of the ICP's of the second period atoms.

Next, a comparison between theory and experiment is in order. If the rms deviation between every pair of experimental and theoretical ICP's is calculated retaining points up to $q=5$ only, then it turns out that none of the three γ-ray ICP's has an rms deviation greater than 0.05 with respect to any of the six CI ICP's. Considering that 1% of $J_0(0)$ or 0.05 is the estimated uncertainty in the experimental ICP's, it seems that the latter are not sufficient to decide which of the CI calculations is the most accurate. If one assumes that the most reliable ICP is the one predicted by the L-CI2E wave function, which we have argued is the most accurate one in this study, then the rms deviations in Table II show that the original 160-keV γ-ray ICP reported by Eisenberger and Reed[29] is the most accurate measured ICP. In fact, the accuracy ordering of the experimental ICP's as determined by closeness to the L-CI2E results is precisely the same as that determined in our previous study.[5] We find it reassuring that each of the experimental ICP's agrees better with L-CI2E than it does[5] with R-CI1.

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	$J_0(0)$	$J_0(0.5)$	$J_0(1.0)$	$J_0(2.0)$	rms (%)[a]	$\Pi_0(0)$	$\Pi_0''(0)$
R-SCF	5.3046	4.3750	2.5549	0.7542	0.492	1.2984	−2.073
L-SCF	5.3491	4.3639	2.5444	0.7550	0.496	1.4075	−2.469
C-SCF	5.3443	4.3646	2.5475	0.7546	0.489	1.4079	−2.772
R-CI1	5.2620	4.3365	2.5583	0.7705	0.346	1.3206	−2.839
R-CI2	5.2703	4.3399	2.5535	0.7700	0.295	1.3208	−2.608
R-CI2E	5.2689	4.3304	2.5495	0.7740	0.260	1.3380	−2.725
L-CI1	5.3138	4.3283	2.5432	0.7710	0.088	1.4281	−2.969
L-CI2	5.3168	4.3302	2.5415	0.7706	0.112	1.4280	−2.932
L-CI2E	5.3069	4.3204	2.5416	0.7746	0.000	1.4319	−3.013
Expt.[b]	5.271	4.309	2.545	0.805	0.41	1.39(.04)	−2.9(1.5)
Expt.[c]	5.325	4.354	2.568	0.805	0.53	1.40(.09)	−2.8(1.0)
Expt.[d]	5.254	4.278	2.526	0.785	0.61	1.40(.17)	−2.7(1.4)
Expt.[e]	5.327	4.286	2.476	0.821	0.77	1.51(.20)	−3.1(1.3)
Expt.[f]	5.399	4.189	2.374	0.720	1.59	1.56(.31)	−4.0(2.0)

[a] rms errors with respect to L-CI2E for $q\leq5$ expressed as a percentage of L-CI2E peak height (5.3069).

[b] 160-keV γ-ray measurements of Ref. 29.

[c] 160-keV γ-ray measurements of Ref. 29, as reanalyzed in Ref. 30.

[d] 60-keV γ-ray measurements of Ref. 31.

[e] X-ray measurements of Ref. 28 as listed in Ref. 29.

[f] 25-keV electron impact measurements of Ref. 32.

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,

$$J_0(q)=J_0(0)-\pi\Pi_0(0)q^2-[\pi\Pi_0''(0)/4]q^4\cdots\ , \tag{2}$$

are of interest as well. Table II shows that the L-CI wave functions predict a $\Pi_0(0)$ markedly closer to the γ-ray values than the R-CI wave functions do. In fact, the uncertainty associated with the $\Pi_0(0)$ value[33] corresponding to the original 160-keV γ-ray ICP[29] is small enough to exclude all the calculations employing the R basis set. The experimental values of $\Pi_0''(0)$ are too uncertain to exclude any of the theoretical values. Comparison of the L-SCF and C-SCF values in Table II shows that $\Pi_0''(0)$ is extremely sensitive to the basis set. The correlation effect on $\Pi_0(0)$ is 1.7%. The correlation effect on $\Pi_0''(0)$ is difficult to estimate since it is smaller than the basis set effect.

C. Moments of the EMD

Moments of the EMD are defined by

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

where the limits on k arise from the p^{-8} asymptotic behavior[37,19] of $\Pi_0(p)$ and the fact that Π_0 is finite and nonzero at $p=0$. Since $\langle p^{-1}\rangle=2J_0(0)$, it has already been considered in Sec. III A. $\langle p\rangle$ is proportional to the Dirac-Slater exchange energy to a high degree of accuracy,[18] and $\langle p^3\rangle$ is roughly proportional[18] to the initial value of the Patterson function of x-ray crystallography. Instead of $\langle p^2\rangle$ and $\langle p^4\rangle$, we list the nonrelativistic kinetic energy given by

$$T_{\mathrm{nr}}=\langle p^2\rangle/2 \tag{4}$$

and the Breit-Pauli correction[38] to it arising from the variation of electron mass with velocity

$$H_{\mathrm{MV}}=-\alpha^2\langle p^4\rangle/8\ , \tag{5}$$

where α is the fine-structure constant. We also consider the full relativistic correction[39] to the nonrelativistic kinetic energy given by

$$H_{\mathrm{RC}}=4\pi\alpha^{-2}\int_0^\infty[(1+\alpha^2p^2)^{1/2}-1-\alpha^2p^2/2]\Pi_0(p)p^2dp. \tag{6}$$

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.[40] Hence, we have made no attempt to extract them from the photon scattering[28–31] ICP's. The moments obtained from electron-impact experiments[32] have rather large uncertainties and cannot[5] even distinguish SCF from CI results.

Thus, only theoretical moments are listed in Table III. 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,[39] only small basis set effects can be detected in Table III for these quantities. $\langle p^{-2}\rangle$ and $\langle p\rangle$ are effectively converged at the CI1 level. 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[1,17–20] the outer regions of the position space natural orbitals.

IV. ANISOTROPIC PROPERTIES

The directional Compton profile (DCP) is given[27] by

$$J(q,\mathbf{q}/q)=\int\Pi(\mathbf{p})\delta(\mathbf{p}\cdot\mathbf{q}/q-q)d\mathbf{p}\ , \tag{7}$$

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

$$\Pi(\mathbf{p})=\Pi(p,\theta) \tag{8}$$

and

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

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.[41,42] Thus,

$$\Pi(p,\theta)=\Pi_0(p)+\Pi_2(p)P_2(\cos\theta)+\Pi_4(p)P_4(\cos\theta)+\cdots\ , \tag{10}$$

$$J(q,\gamma)=J_0(q)+J_2(q)P_2(\cos\gamma)+J_4(q)P_4(\cos\gamma)+\cdots\ , \tag{11}$$

TABLE III. Properties of the isotropic momentum density.

Wave function	$\langle p^{-2}\rangle$	$\langle p\rangle$	$\langle p^3\rangle$	T_{NR}	H_{MV}	H_{RC}
R-SCF	15.920	38.083	2265.4	108.871	−0.298 89	−0.268 10
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
R-CI1	15.809	38.294	2268.2	109.302	−0.298 85	−0.268 08
R-CI2	15.858	38.281	2268.2	109.294	−0.298 85	−0.268 08
R-CI2E	15.914	38.334	2270.4	109.452	−0.299 05	−0.268 26
L-CI1	16.370	38.241	2267.7	109.211	−0.299 25	−0.268 33
L-CI2	16.384	38.235	2267.7	109.205	−0.299 24	−0.268 33
L-CI2E	16.361	38.294	2269.8	109.366	−0.299 39	−0.268 47

TABLE IV. Anisotropic properties of the electron momentum density.

Wave function	$J(0,0)$	$J(0,\pi/2)$	$J_2(0)$	$J_4(0)$	$J_6(0)$	ΔT	$\Pi_2(0.5)$
R-SCF	5.8499	5.3385	0.1120	0.3004	0.0904	0.1988	−0.1274
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
R-CI1	5.7452	5.3156	0.0649	0.2885	0.0883	0.1621	−0.0941
R-CI2	5.7588	5.3241	0.0660	0.2912	0.0893	0.1626	−0.1007
R-CI2E	5.7580	5.3212	0.0704	0.2911	0.0866	0.1601	−0.1050
L-CI1	5.8492	5.3372	0.1149	0.2773	0.0943	0.0064	−0.1174
L-CI2	5.8545	5.3414	0.1138	0.2798	0.0953	0.0023	−0.1181
L-CI2E	5.8448	5.3306	0.1163	0.2797	0.0937	−0.0043	−0.1171

where the P_L are Legendre polynomials, the leading terms of expansions (10) and (11) are the isotropic EMD and ICP, respectively, and the partial waves are related[41] by

$$J_L(q)=2\pi \int_{|q|}^{\infty} \Pi_L(p)P_L(q/p)p\,dp \;. \tag{12}$$

Note that the DuMond relation, Eq. (1), is the $L=0$ case of Eq. (12). A quantity of great chemical interest[43] is the anisotropy of the kinetic energy tensor given by

$$\Delta T=\langle p^2P_2(\cos\theta)\rangle/2 \tag{13a}$$

$$=(2\pi/5)\int_0^{\infty} \Pi_2(p)p^4dp \;. \tag{13b}$$

TABLE V. L-CI2E momentum density and Compton profiles.

q	$\Pi_0(q)$	$J_0(q)$	$J(q,0)$	$J(q,\pi/2)$
0.0	1.4319	5.3069	5.8448	5.3306
0.1	1.4169	5.2622	5.7562	5.2864
0.2	1.3725	5.1308	5.5055	5.1559
0.3	1.3009	4.9208	5.1334	4.9452
0.4	1.2060	4.6453	4.6914	4.6655
0.5	1.0937	4.3204	4.2277	4.3325
0.6	0.9708	3.9642	3.7775	3.9652
0.7	0.8446	3.5941	3.3607	3.5834
0.8	0.7218	3.2259	2.9850	3.2047
0.9	0.6072	2.8721	2.6509	2.8434
1.0	0.5041	2.5416	2.3551	2.5091
1.2	0.3370	1.9699	1.8629	1.9400
1.4	0.2193	1.5241	1.4816	1.5050
1.6	0.1409	1.1914	1.1902	1.1845
1.8	0.0905	0.9493	0.9695	0.9518
2.0	0.0588	0.7746	0.8020	0.7828
2.2	0.0390	0.6479	0.6733	0.6585
2.4	0.0267	0.5545	0.5725	0.5650
2.6	0.0190	0.4837	0.4924	0.4929
2.8	0.0141	0.4283	0.4280	0.4355
3.0	0.0109	0.3833	0.3762	0.3886
3.5	0.0065	0.2985	0.2865	0.2999
4.0	0.0044	0.2361	0.2314	0.2356
4.5	0.0031	0.1872	0.1905	0.1862
5.0	0.0022	0.1482	0.1542	0.1474
6.0	0.0012	0.0927	0.0935	0.0925
7.0	0.0006	0.0584	0.0574	0.0583
8.0	0.0003	0.0372	0.0376	0.0371
9.0	0.0002	0.0240	0.0242	0.0240
10.0	0.0001	0.0158	0.0156	0.0157

Table IV lists peak values of the DCP's parallel and perpendicular to the molecular axis calculated directly from Eq. (7) as in Ref. 35, 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. Basis set effects are quite large for all these properties and basis R is inadequate[5] for them. Comparison of the L-SCF and C-SCF results suggests that basis L is probably adequate except for ΔT and $\Pi_2(0.5)$. Correlation effects on $J(0,\gamma)$ were found to decrease as γ increases from 0 to $\pi/2$, in agreement with our previous work.[5] Table IV suggests that the CI1 (i.e., first-order[10]) level is sufficient to obtain DCP's to approximately 0.5% which should be accurate enough for all practical purposes.

An indication of the convergence of expansion (11) is obtained from Table IV by noting that

$$J(q,0)=J_0(q)+J_2(q)+J_4(q)+J_6(q)+\cdots \tag{14}$$

because[44] $P_L(1)=1$ for all L. Thus, for L-CI2E the sum of $J_L(0)$ for all $L>6$ is 0.048 of which 0.03 comes from $J_8(0)$.

V. CONCLUDING REMARKS

Table V lists the DCP's parallel and perpendicular to the internuclear axis, along with the ICP and isotropic EMD, as predicted by the L-CI2E wave function. These values supercede our previous results;[5] the Compton profiles have probably converged to 0.005 with respect to both basis set and electron correlation except at very large q where they are dominated by contributions from the core electrons which were uncorrelated in this work. The impulse approximation probably contributes further errors of the same magnitude. Corrections for vibrational motion and for our use of a bond length slightly shorter than the current experimental value[12] would jointly contribute errors of no more than 0.005 in the Compton profiles and 0.001 in the isotropic EMD.[5]

The kinetic energy anisotropy ΔT is so small in magnitude (the best estimate in Table IV is −0.004) that substantially larger basis sets and a more elaborate description of correlation, including core electrons, would be required to obtain an accurate value and even its sign.

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