Closed-form analytical solutions for the calculation of the moments of the molecular electron density

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Moments of the molecular electron density can be related directly to several experimental observables, but formerly they have only been accurately calculated through methods which lack consistency with standard quantum chemical methods. Here we report analytical solutions to the basic molecular integrals required to compute the moments of the molecular electron charge density over Gaussian basis functions. These are derived and cast into a practical closed form, suitable to interface with modern codes for the calculation of the molecular electronic structure. Illustrative calculations for the hydrogen molecule, at both the Hartree–Fock and the full configuration interaction levels of theory, are shown and discussed in connection with observables linked directly to some of the calculated moments.

1. Introduction

The calculation of accurate wavefunctions for small molecules has been made possible by the impressive progress in electronic structure theory and computer technology. Less accurate, but still very useful, wavefunctions can also be obtained for larger molecules. However, for most applications of quantum mechanics it is necessary to compute expectation values of density functions in terms of which the properties of interest are given as averaged values. This requirement is closely connected with one of the major challenges of quantum mechanics: the development of practical procedures for the extraction of useful information from N-electron wavefunctions.

In this paper, we will sketch how the moments of the electron density function can be calculated analytically for an N-electron wavefunction that has been expanded in terms of Gaussian basis function sets. Our formulae represent an alternative derivation to that of Wang and Smith [16], who reported also the equations to calculate the radial moments in the momentum space.

It is well know that various moments of the electron density function are closely related with measurable magnitudes [2]. In particular, the moment of order -1 is proportional to the diamagnetic shielding factor [5], and the diamagnetic susceptibility [9] is found to be proportional to the moment of order 2. Also, there is some evidence [8] that the moment of order 3 is related to the averaged electron density in momentum space, which can be measured through the reciprocal form factor [4].

Thus, we see that the moments of the electron density function are not only relevant in building an understanding of basic chemical concepts, but are also related to numerous experimental observables, thereby linking even more closely the theoretical and experimental fields.

2.   Method

The ith order moment of the spherically averaged electron density is defined as

$$\langle r^i \rangle = \int r^i \rho(r) \, \mathrm{d}r, \tag{1}$$

where $\rho(r)$ is the spherically averaged electron density

$$\rho(r) = \int \rho(\mathbf{r}) r^2 \sin \theta \, \mathrm{d}\phi \, \mathrm{d}\theta. \tag{2}$$

The electron density $\rho(\mathbf{r})$ is a one-electron reduction of $\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$, the electronic wavefunction of the N-electron system (atom or molecule):

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} \langle \Psi | \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle. \tag{3}$$

The electronic wavefunction Ψ can be obtained from several approximations (HF, CI, etc.), and the electron density is then calculated in terms of the natural orbitals $\{\phi_\mu(\mathbf{r})\}$ as

$$\rho(\mathbf{r}) = \sum_{\mu,\nu} P_{\mu\nu} \phi_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}), \tag{4}$$

where $P_{\mu\nu}$ is the (μ, ν) element of the density matrix.

Customarily the natural orbitals are expanded in terms of Gaussian-type primitives as

$$\phi_\mu(\mathbf{r}) = \sum_A c_A G_A(\mathbf{r}). \tag{5}$$

This leads us to write equation (1) in the form

$$\langle r^i \rangle = \sum_{\mu,\nu} P_{\mu\nu} \sum_{A,B} c_A c_B \int r^i G_A(\mathbf{r}) G_B(\mathbf{r}) r^2 \sin \theta \, \mathrm{d}\phi \, \mathrm{d}\theta \, \mathrm{d}r, \tag{6}$$

where $G_C(\mathbf{r})$ is a Cartesian Gaussian function defined as

$$G_C(\mathbf{r}) \equiv G_C(\mathbf{r}; \alpha, \mathbf{R}_C, l, m, n) = (x - X_C)^l (y - Y_C)^m (z - Z_C)^n \, \mathrm{e}^{-\alpha |\mathbf{r} - \mathbf{R}_C|^2}. \tag{7}$$

Therefore, the integral in equation (6) can be written as

$$I(i) = \int r^i G_A(\mathbf{r}; \alpha_1, \mathbf{R}_A, l_1, m_1, n_1) G_B(\mathbf{r}; \alpha_2, \mathbf{R}_B, l_2, m_2, n_2) r^2 \sin \theta \, \mathrm{d}\phi \, \mathrm{d}\theta \, \mathrm{d}r, \tag{8}$$

which, using the Gaussian functions contraction theorem [12], can be cast as

$$I(i) = K \sum_{l=0}^{l_1+l_2} \sum_{m=0}^{m_1+m_2} \sum_{l=0}^{n_1+n_2} f_l f_m f_n$$
$$\times \int r^i (x - X_P)^l (y - Y_P)^m (z - Z_P)^n \, e^{-\gamma |\mathbf{r} - \mathbf{R}_P|^2} r^2 \sin\theta \, d\phi \, d\theta \, dr, \quad (9)$$

where

$$K = e^{-\alpha_1 \alpha_2 |\mathbf{R}_A - \mathbf{R}_B|^2 / (\alpha_1 + \alpha_2)}, \tag{10}$$

$$\gamma = \alpha_1 + \alpha_2, \tag{11}$$

$$\mathbf{R}_P = \frac{\alpha_1 \mathbf{R}_A + \alpha_2 \mathbf{R}_B}{\gamma}. \tag{12}$$

For atomic calculations, $\mathbf{R}_P \equiv (X_P, Y_P, Z_P) = 0$, and the integral in equation (9) reduces to

$$I_1(i) = \int r^i x^l y^m z^n \, e^{-\gamma |\mathbf{r}|^2} r^2 \sin\theta \, d\phi \, d\theta \, dr. \tag{13}$$

Expressing the Cartesian coordinates in terms of spherical coordinates we get

$$I_1(i) = \int_0^\infty r^{i+l+m+n+2} e^{-\gamma r^2} \, dr$$
$$\times \int_0^\pi (\sin\theta)^{l+m+1} (\cos\theta)^n \, d\theta \int_0^{2\pi} (\cos\phi)^l (\sin\phi)^m \, d\phi. \tag{14}$$

The angular integrals can be solved in terms of the Beta-function, $B(x, y)$, as

$$\int_0^{2\pi} (\cos\phi)^l (\sin\phi)^m \, d\phi = \begin{cases} 2B((l+1)/2, (m+1)/2) & \text{if } l \text{ and } m \text{ even,} \\ 0 & \text{otherwise,} \end{cases} \tag{15}$$

$$\int_0^\pi (\sin\theta)^{l+m+1} (\cos\theta)^n \, d\theta = \begin{cases} B((l+m+2)/2, (n+1)/2) & \text{if } n = \text{even,} \\ 0 & \text{if } n = \text{odd,} \end{cases} \tag{16}$$

and the radial integral is

$$\int_0^\infty r^{k+2} e^{-\gamma r^2} \, dr = \begin{cases} \frac{(k+1)!!}{2(2\gamma)^{(k+2)/2}} \sqrt{\frac{\pi}{\gamma}} & \text{if } k = \text{even,} \\ \frac{((k+1)/2)!}{2(\gamma)^{((k+1)/2+1)}} & \text{if } k = \text{odd,} \end{cases} \tag{17}$$

with $k = i + l + m + n$, which completes the derivation of the necessary analytical formulae to evaluate $\langle r^i \rangle$ for atomic systems.

For molecular calculations, if the molecule is linear, we can take the nuclei lying on the z-axis so that $X_P = Y_P = 0$ and $Z_P = \mathbf{R}_P$. If the molecule is not linear a coordinate transformation can be defined for any pair of nuclei in order to get $\mathbf{R}_P$ on

the z-axes, as described in [15]. In either case, the integral of equation (9) takes the form

$$I_1(i) = \int r^i x^l y^m (z - R_P)^n \, \mathrm{e}^{-\gamma |\mathbf{r} - \mathbf{R}_P|^2} r^2 \sin\theta \, \mathrm{d}\phi \, \mathrm{d}\theta \, \mathrm{d}r. \tag{18}$$

Expressing the Cartesian coordinates in terms of the spherical coordinates,

$$I_1(i) = \int r^i (r \sin\theta \cos\phi)^l (r \sin\theta \sin\phi)^m (r \cos\theta - R_P)^n$$

$$\times \, \mathrm{e}^{-\gamma(r^2 + R_P^2 - 2rR_P \cos\theta)} r^2 \sin\theta \, \mathrm{d}\phi \, \mathrm{d}\theta \, \mathrm{d}r, \tag{19}$$

and working out the binomial we get

$$I_1(i) = \sum_{s=0}^{n} \binom{n}{s} (-R_P)^{n-s}$$

$$\times \int_0^\infty \left[\int_0^\pi \mathrm{e}^{2\gamma r R_P \cos\theta} (\sin\theta)^{l+m+1} (\cos\theta)^s \, \mathrm{d}\theta \right] r^{i+l+m+s+2} \, \mathrm{e}^{-\gamma(r^2 + R_P^2)} \, \mathrm{d}r$$

$$\times \int_0^{2\pi} (\cos\phi)^l (\sin\phi)^m \, \mathrm{d}\phi. \tag{20}$$

The integration over ϕ has been solved earlier (see equation (15)), and the integral over θ can be written as

$$\int_0^\pi \mathrm{e}^{2\gamma r R_P \cos\theta} (\sin\theta)^{l+m+1} (\cos\theta)^s \, \mathrm{d}\theta$$

$$= \sum_{t=0}^{(l+m)/2} \binom{(l+m)/2}{t} (-1)^{(l+m)/2-t} \int_0^\pi \mathrm{e}^{2\gamma r R_P \cos\theta} (\cos\theta)^{l+m+s-2t} \sin\theta \, \mathrm{d}\theta, \tag{21}$$

so that the integral

$$\int_0^\pi \mathrm{e}^{2\gamma r R_P \cos\theta} (\cos\theta)^{l+m+s-2t} \sin\theta \, \mathrm{d}\theta = \int_{-1}^1 \mathrm{e}^{a\mu} \mu^q \, \mathrm{d}\mu, \tag{22}$$

with $a = 2\gamma r R_P$, $q = l + m + s - 2t$ and $\mu = \cos\theta$, can be solved as

$$\int_{-1}^1 \mathrm{e}^{a\mu} \mu^q \, \mathrm{d}\mu = \mathrm{e}^a \left(\frac{1}{a} + \sum_{u=1}^q \frac{(-1)^u q!}{(q-u)! a^{u+1}} \right)$$

$$- (-1)^q \mathrm{e}^{-a} \left(\frac{1}{a} + \sum_{u=1}^q \frac{q!}{(q-u)! a^{u+1}} \right), \tag{23}$$

which, substituting in equation (20), leads to

$$I_1(i) = 2B\left(\frac{l+1}{2}, \frac{m+1}{2} \right) \sum_{s=0}^n \binom{n}{s} (-R_P)^{n-s} \sum_{t=0}^{(l+m)/2} \binom{(l+m)/2}{t} (-1)^{(l+m)/2-t}$$

$$\times \left[\frac{S(v)}{2\gamma R_P} + \sum_{u=1}^{q} \frac{S(v-u)(-1)^u(q)!}{(q-u)!(2\gamma R_P)^{u+1}} \right.$$
$$\left. + (-1)^{q+1} \left(\frac{R(v)}{2\gamma R_P} + \sum_{u=1}^{q} \frac{R(v-u)(q)!}{(q-u)!(2\gamma R_P)^{u+1}} \right) \right], \tag{24}$$

where $v = i + l + m + s + 1$.

The integrals over r are included in the $S(u)$ and $R(u)$ integral functions, namely,

$$S(u) = \int_0^\infty e^{-\gamma(r-R_P)^2} r^u \, dr \tag{25}$$

and

$$R(u) = \int_0^\infty e^{-\gamma(r+R_P)^2} r^u \, dr. \tag{26}$$

These two integrals can be solved, for any positive integer u, using the following recurrence relations:

$$S(u+2) = \int_0^\infty e^{-\gamma(r-R_P)^2} r^{u+2} \, dr = \frac{u+1}{2\gamma} S(u) + R_P S(u+1) \tag{27}$$

and

$$R(u+2) = \int_0^\infty e^{-\gamma(r+R_P)^2} r^{u+2} \, dr = \frac{u+1}{2\gamma} R(u) - R_P R(u+1). \tag{28}$$

The initial integrals in these recurrence relations, $S(0)$, $S(1)$, $R(0)$ and $R(1)$, can be expressed in terms of the error function:

$$S(0) = \int_0^\infty e^{-\gamma(r-R_P)^2} \, dr = \frac{1}{2}\sqrt{\frac{\pi}{\gamma}} \left[1 + \mathrm{er} f\left(\sqrt{\gamma} R_P\right) \right], \tag{29}$$

$$S(1) = \int_0^\infty e^{-\gamma(r-R_P)^2} r \, dr = \frac{e^{-\gamma R_P^2}}{2\gamma} + \frac{R_P}{2}\sqrt{\frac{\pi}{\gamma}} \left[1 + \mathrm{er} f\left(\sqrt{\gamma} R_P\right) \right], \tag{30}$$

$$R(0) = \int_0^\infty e^{-\gamma(r+R_P)^2} \, dr = \frac{1}{2}\sqrt{\frac{\pi}{\gamma}} \left[1 - \mathrm{er} f\left(\sqrt{\gamma} R_P\right) \right], \tag{31}$$

$$R(1) = \int_0^\infty e^{-\gamma(r+R_P)^2} r \, dr = \frac{e^{-\gamma R_P^2}}{2\gamma} - \frac{R_P}{2}\sqrt{\frac{\pi}{\gamma}} \left[1 - \mathrm{er} f\left(\sqrt{\gamma} R_P\right) \right], \tag{32}$$

which closes the required formulae for the analytical evaluation of $\langle r^i \rangle$ for molecules.

3. Some illustrative calculations

The formulae shown in the preceding section can be coded easily and interfaced with modern efficient molecular electronic structure calculation programs, such as

Table 1
FCI (HF in italics) moments and total energy in atomic units of the spherically averaged electron density for the H_2 molecule using various basis sets. The origin has been set at the center of the molecule.

Order	B0	B1	B2	B3	B4	B5	B6
−1	1.914739	1.917454	1.914101	1.910730	1.916441	1.913102	1.913375
	1.911377	*1.909367*	*1.909292*	*1.907684*	*1.907668*	*1.907037*	*1.906721*
0	2.000053	2.000009	1.914101	2.000028	2.000028	2.000056	1.998412
	1.999977	*1.999953*	*1.999957*	*2.000010*	*2.000061*	*2.000069*	*1.999205*
1	2.856128	2.854300	2.861320	2.869891	2.862641	2.866866	2.861767
	2.860889	*2.872059*	*2.874554*	*2.879659*	*2.880966*	*2.882979*	*2.880697*
2	5.214235	5.200457	5.225693	5.263443	5.238950	5.249999	5.236428
	5.229288	*5.270138*	*5.282531*	*5.307076*	*5.312057*	*5.318250*	*5.312242*
3	11.709248	11.611218	11.687280	11.832864	11.757047	11.783115	11.746226
	11.754194	*11.849019*	*11.898819*	*12.003038*	*12.017539*	*12.036369*	*12.019832*
4	31.448931	30.825287	31.046074	31.616342	31.367757	31.448972	31.342634
	31.609822	*31.648965*	*31.844004*	*32.294449*	*32.329797*	*32.410143*	*32.361317*
Energy	−1.154322	−1.168892	−1.171385	−1.171830	−1.173309	−1.173752	−1.173973
	−1.128467	*−1.132899*	*−1.133344*	*−1.133489*	*−1.133496*	*−1.133594*	*−1.133595*

Table 2
FCI (HF in italics) moments and total energy in atomic units of the spherically averaged electron density for the H_2 molecule using various basis sets. The origin has been set at a proton.

Order	B0	B1	B2	B3	B4	B5	B6
−1	1.816142	1.824597	1.823614	1.823433	1.824406	1.825100	1.823804
	1.806592	*1.814425*	*1.815357*	*1.815654*	*1.815654*	*1.816292*	*1.815471*
0	2.000053	2.000009	2.000016	2.000028	2.000028	2.000056	1.998434
	1.999977	*1.999953*	*1.999957*	*2.000010*	*2.000061*	*2.000069*	*1.999205*
1	3.126944	3.100514	3.102088	3.102581	3.099247	3.098886	3.096538
	3.132590	*3.113335*	*3.111690*	*3.110915*	*3.110934*	*3.111016*	*3.110194*
2	6.194260	6.088432	6.093361	6.094236	6.080207	6.078247	6.074373
	6.209277	*6.140380*	*6.133583*	*6.128302*	*6.128209*	*6.128245*	*6.128024*
3	14.778917	14.404189	14.413526	14.414530	14.362904	14.358915	14.351571
	14.821170	*14.599499*	*14.574522*	*14.551347*	*14.549658*	*14.553619*	*14.556216*
4	41.349240	39.918487	39.914518	39.929073	39.732964	39.750803	39.734431
	41.502812	*40.675156*	*40.587671*	*40.514026*	*40.497863*	*40.548523*	*40.561956*
Energy	−1.154322	−1.168892	−1.171385	−1.171830	−1.173309	−1.173752	−1.173973
	−1.128467	*−1.132899*	*−1.133344*	*−1.133489*	*−1.133496*	*−1.133594*	*−1.133595*

Gaussian [3] or GAMESS [1,13]. This allows one to calculate the moments of the electronic charge density function, up to an arbitrary order, using the very accurate wavefunctions provided by these programs. Thus, in tables 1 and 2, we present the calculated values of $\langle r^n \rangle$ with $n = -1, 0, 1, 2, 3, 4$, for the hydrogen molecule at the full configuration interaction (FCI) level of theory with seven different basis sets of increasing size yielding progressively better energies. B0 is the (9s/4s) contracted
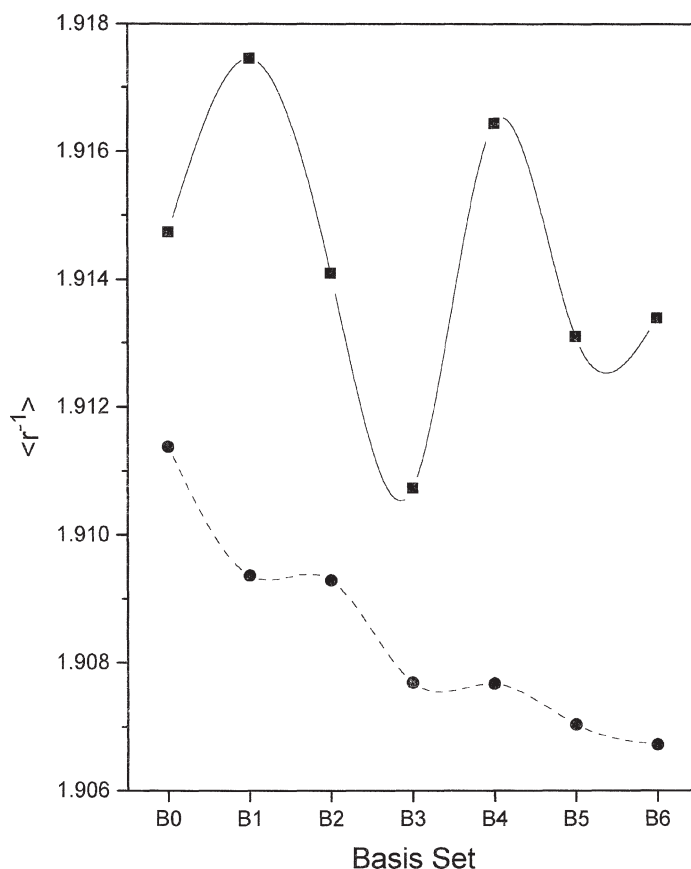
Figure 1. FCI (solid line) and HF (dashed line) calculated values of $\langle r^{-1} \rangle$ for a number of basis sets of increasing quality.

Gaussian-type orbital (GTO) basis set of Siegbahn and Liu [14], which has a basis set incompleteness for the hydrogen atom of only 2 μhartree. Basis sets B1–B6 correspond to the B0 basis set augmented by a series of nuclear-centered polarization functions, namely, 1p, 2p, 3p, 3p1d, 3p2d and 3p2d1f, whose exponents have been given by Wright and Barclay [17]. Notice that, for the largest basis set (B6), the FCI energy of the H$_2$ molecule differs only by 0.5 mhartree with respect to the exact energy of Kolos and Wolniewicz [7]. Nevertheless, it is worthwhile to point out that the FCI energy of the H$_2$ converges monotonically to the exact result with increasing the number of added polarization functions.

Inspection of tables 1 and 2 reveals that FCI and HF calculated moments have a very different behaviour with respect to the increasing "energy" quality of the wave-function. Thus, while the HF moments do show a well behaved monotonic behaviour, decreasing for $\langle r^{-1} \rangle$ and increasing for $\langle r^{n} \rangle$, $n \geqslant 1$, with respect to the quality of the basis set, the corresponding FCI moments show a damped oscillatory behavior. This is better illustrated in figures 1 and 2. This curious feature, though visible in earlier
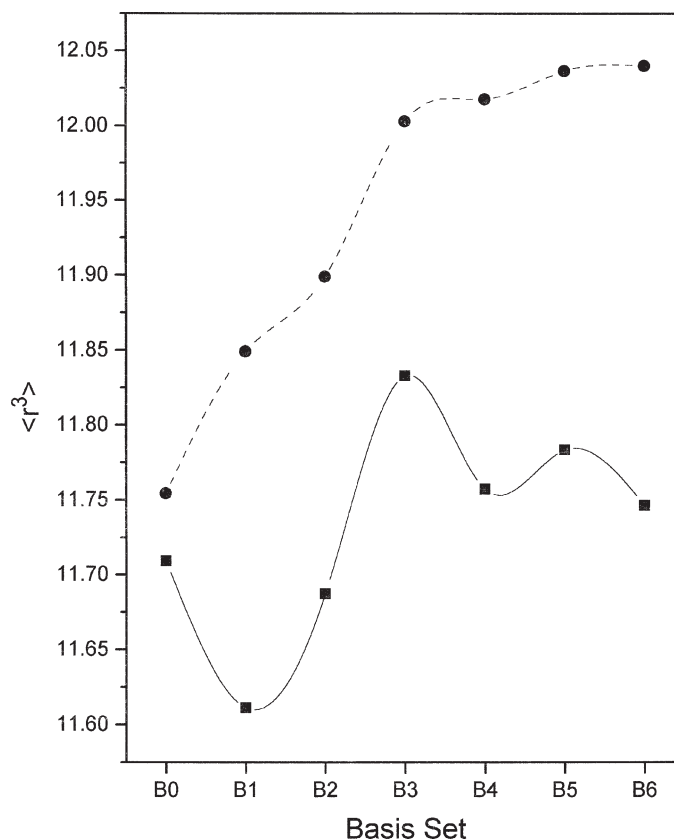
Figure 2. FCI (solid line) and HF (dashed line) calculated values of $\langle r^3 \rangle$ for a number of basis sets of increasing quality.

calculations on both atoms [5] and molecules [6], has gone without remark. Notice that this dumped oscillatory behavior is apparently related with the increasing amount of electron correlation recovered by wavefunctions. In our calculation on the hydrogen molecule, the oscillatory behavior appears to be dependent on the angular moment of the polarization basis functions added, where the first set of functions of higher angular momentum increases (decreases) the calculated value of $\langle r^{-1} \rangle$ ($\langle r^n \rangle$, $n \geqslant 1$), and additional functions with the same angular momentum have the opposite effect.

As emphasized in the introduction, some of these moments are directly related to experimentally measurable magnitudes. Namely, magnetic properties like the nuclear diamagnetic shielding factor is determined by the formula

$$\sigma^{\mathrm{d}} = \frac{1}{3}\alpha^2 \langle r^{-1} \rangle, \tag{33}$$

and the molar diamagnetic susceptibility is defined by

$$\chi^{\mathrm{d}} = -\frac{1}{6}N_{\mathrm{Av}}\alpha^2 a_0^3 \langle r^2 \rangle, \tag{34}$$

where α is fine-structure constant, N_{Av} is Avogadro's constant and a_0 is the Bohr radius. Using the values for α, N_{Av} and a_0 reported by Pyykkö and Zhao [10] our best estimation for σ^d is

$$\sigma^d = 3.237 \times 10^{-5} \text{ a.u.,} \tag{35}$$

which compares very well with the experimental value [11] of 3.21 ± 0.04 a.u. and favorably with respect to a number of earlier calculations [2, p. 112].

Our best estimates for the diamagnetic susceptibility, χ^d, are

$$\chi^d = -4.1473 \times 10^{-6} \text{ cm}^3/\text{mol} \tag{36}$$

for the origin of the vector potential at the center of the molecule, and

$$\chi^d = -4.8110 \times 10^{-6} \text{ cm}^3/\text{mol} \tag{37}$$

for the origin of the vector potential at a proton. These two values compare well with their corresponding experimental estimates [11] of -4.110 ± 0.04 cm^3/mol and -4.886 ± 0.04 cm^3/mol, respectively, as well as with several earlier calculations [2, p. 101]. Thus our methods provide data that matches well with experimental observables while maintaining high quality energy predictions and compatibility with well-known quantum chemistry methods.

4. Summary

Practical closed-form analytical solutions of the basic molecular integrals required to evaluate the moments of the electron charge density functions have been derived for the Gaussian expansion of the molecular orbitals. The derived formulae, which can be easily coded and interfaced with modern electronic structure calculation programs, will help to learn more about the quality of the wavefunction and the effects of the size of the basis set, on both the ground and excited states of molecules. Also, they can be used to assess the behavior of various electron density functionals, both pure and hybrid, as well as to determine the effects of the solvent on magnitudes depending on average values of powers of the electron coordinate, like the diamagnetic nuclear shielding constant, the diamagnetic susceptibility and the electric quadrupole moment.

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