Journal of Mathematical Chemistry 21 (1997) 211–222

Two-center p-space integrals: diatomic molecular moments

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Received 12 September 1996; revised 19 February 1997

Analytical expressions for the calculation of both orbital and total moments of diatomic molecules using Gaussian-type orbitals are formulated. Moments $\langle p^t \rangle$ with $-2 \leqslant t \leqslant 4$ are computed for the ground state of 35 diatomic molecules at equilibrium bond length using 6-311$G(d,p)$ basis sets. In order to test our expressions, these expectation momentum values are compared with the values calculated using self-consistent-field wave functions of Hartree–Fock quality, which give Hartree–Fock limit energies.

1. Introduction

It is well known that the electron density can be expressed as a function of the momenta of the electrons rather than as a function of their position. Momentum space is very convenient for the interpretation of the Compton and $(e, 2e)$ scattering experiments [10,49]. For comparison with experimental data, theoretical momentum expectation values for atoms and molecules are needed. The powers of atomic moments are directly related to some properties (Compton profile, Slater–Dirac exchange energy, electron kinetic energy, Patterson function, relativistic energy). They also show strong periodic variation and have received our attention in recent years [21,22,24–26].

The studies of atoms have played an important role both in the development of experimental techniques and in testing the validity of theoretical approximations of the electron momentum density properties. In recent years, Smith et al. [18,43, 45,46] have studied the influence of electron correlation in the wave function on the electron momentum density and other related density properties. They have computed moments from the density previously obtained in r-space. The details of the theoretical methodology are well described in earlier papers, using an elegant formalism [7,8]. Relativistic contributions to the scattering factors of the first- and second-row atoms and ions have been also tabulated [48].

However, momentum space concepts have been scarcely used in chemistry [17, 40]. Allan and Cooper have suggested that momentum space concepts provide a novel route for the quantitative estimation of molecular similarity [4,15]. Their approach involves a comparison of the p-space electron densities $\rho(p)$ which are calculated for the molecules, the orbitals, or molecular fragments of interest. Orbital momentum densities of CO, NO and O_2 have been calculated at the Hartree–Fock level [44]. The expectation values $\langle p^4 \rangle$ of several small molecules using near HF limit basis sets have been computed by Davidson et al. [19]. Allan et al. [5] have reported that the test for the relation $\langle p^t \rangle = \int \rho(r)^{1+(1/3)t}\,\mathrm{d}r$ ($t = -1, 1$ and 2) with HF limit wavefunctions for eleven diatomic molecules and two singly charged positive ions, shows changes of 10% in the proportional constants.

Allan and Cooper [3] have studied the effects of the bond formation in the electronic density in both momentum and position-spaces for some diatomic molecules over a wide range of nuclear separation and used the truncated gradient expansion for obtaining accurate momentum expectation values [2,6]. Moreover, they have calculated electron momentum densities for π electrons of one-dimensional regular chain of polyenes [16]. Ramírez studied the electron momentum densities of diatomic molecules and also discussed the chemical bonding through the bond directional principle and the density difference maps [38,39]. A more detailed topological analysis of electron momentum densities of the first-row hydrides and homonuclear diatomic molecules using HF limit wavefunctions has been carried out [47]. The momentum space representation has recently been employed for localized molecular orbitals in hydrocarbons, boranes and transition metal complexes [33]. The experimental momentum profiles have been compared with theoretical spherically averaged momentum profiles from several basis sets obtained at different levels of calculations for the NO and O_2 molecules [42].

However, theoretical calculations require the use of near-Hartree–Fock basis sets to obtain valence electron densities which fit in the experimental data [50]. It appears that the correlation effects will generally be smaller than the uncertainties of the experimental data obtained from X-ray diffraction [9].

The general expressions for two-center p-space integrals using Gaussian type orbitals (GTOs) are detailed in section 2, and their implementation for the computation of the moments of diatomic molecules is discussed in section 3.

2. Two-center p-space integrals for GTOs

The momentum expectation values $\langle p^t \rangle$ for a molecule are given by the integral

$$\langle p^t \rangle = \left\langle \Psi \middle| \sum_i^N p_i^t \middle| \Psi \right\rangle. \tag{1}$$

Using the Hartree–Fock description of a molecular system with N-electrons the wave function Ψ is written as

$$\Psi = \frac{1}{\sqrt{N!}} \sum_{p=1}^{N!} (-1)^p P(\Phi_1, \Phi_2, \ldots, \Phi_N), \tag{2}$$

P being a permutation operator and $\{\Phi_i\}_{i=1}^{N}$ being the set of molecular orbitals (MOs). Under the linear combination of atomic orbitals (LCAO) approximation the MOs are expanded in a non-complete basis set $\{\varphi_i\}_{i=1}^{m}$

$$\Phi_j(r,\theta,\phi) = \sum_{s=1}^{m} c_{sj}\varphi_s(r,\theta,\phi). \tag{3}$$

Taking into account that the p operator is monoelectronic, the integral in equation (1) can be written as

$$\langle p^t\rangle = \sum_{j=1}^{N} \langle \Phi_j|p^t|\Phi_j\rangle \equiv \sum_{j=1}^{N}\langle p^t\rangle_j. \tag{4}$$

That is, the molecular momentum expectation values can be obtained from the addition of orbital momentum expectation values $\langle p\rangle_j$, which are related to integrals over basis functions:

$$\langle p^t\rangle_j = \sum_{r,s}^{m} c_{rj}c_{sj}\langle \varphi_r(r,\theta,\phi)|p^t|\varphi_s(r,\theta,\phi)\rangle. \tag{5}$$

For the evaluation of the above integrals the Fourier transform of basis set functions must be introduced

$$\widehat{\varphi}(p,\theta_p,\phi_p) = \frac{1}{(2\pi)^{3/2}}\int \mathrm{d}^3\mathbf{r}\,\mathrm{e}^{-\mathrm{i}\mathbf{r}\mathbf{p}}\varphi(r,\theta,\phi). \tag{6}$$

The cartesian GTO functions are defined as

$$\varphi_{n,l}^{m}(r,\theta,\phi) = B(n,\alpha)r^{n-1}\mathrm{e}^{-\alpha r^2}Z_{l,m}(\theta,\phi). \tag{7}$$

n, l and m are the principal, angular and magnetic quantum numbers, respectively; α is the exponent, and $B(n,\alpha)$ is the normalization constant:

$$B(n,\alpha) = \left[\frac{2(2\alpha)^{(n+1/2)}}{\Gamma(n+1/2)}\right]^{1/2}. \tag{8}$$

The $Z_{l,m}(\theta,\phi)$ normalized real harmonics are defined by

$$Z_{l,m}(\theta,\phi) = \sqrt{\frac{(2l+1)(l-|m|)!}{2\pi(1+\delta_{m0})(l+|m|)!}}(-1)^m P_l^{|m|}(\cos\theta)f_m(\phi), \tag{9}$$

where $f_m(\phi) = \cos m\phi$ if $m \geqslant 0$ and $f_m(\phi) = \sin|m|\phi$ if $m < 0$; $P_l^{|m|}(\cos\theta)$ is the unnormalized associated Legendre function [27].

Kaijser and Smith [28] have demonstrated that the Fourier transform, when $n = l+1$, can be written as

$$\widehat{\varphi}_{n,l}^{m}(p,\theta_p,\phi_p) = (-\mathrm{i})^l\frac{B(n,\alpha)}{(2\alpha)^{(n+1/2)}}\mathrm{e}^{-\mathrm{i}\mathbf{p}\mathbf{A}}p^{(n-1)}\mathrm{e}^{-p^2/(4\alpha)}Z_{l,m}(\theta_p,\phi_p), \tag{10}$$

where **A** is the position vector of the nucleus in which the studied function is centered in the frame of the molecular coordinate system.

Standard molecular calculations use 6 Cartesian d Gaussian functions. This implies that the s component in the momentum space is also needed and it can be expressed as

$$\widehat{\varphi}^{0}_{3,0}(p,\theta_p,\phi_p)=\frac{B(3,\alpha)}{(2\alpha)^{(7/2)}}\mathrm{e}^{-\mathrm{i}\mathbf{pA}}\,\mathrm{e}^{-p^2/(4\alpha)}(-p^2-6\alpha)Z_{0,0}(\theta_p,\phi_p). \tag{11}$$

Due to the monoelectronic nature of the p operator, the integrals required in equation (5) are divided into two groups: one and two-center integrals. The solution of the former was given by the authors [23] and according to the definition of basis sets presented here can be written as

$$\left\langle\widehat{\varphi}^{m_1}_{n_1,l_1}|p^t|\widehat{\varphi}^{m_2}_{n_2,l_2}\right\rangle=\frac{B(n_1,\alpha_1)B(n_2,\alpha_2)}{(2\alpha_1)^{(n_1+1/2)}(2\alpha_2)^{(n_2+1/2)}}\delta_{l_1,l_2}\delta_{m_1,m_2}I(n_1,n_2,\alpha_1,\alpha_2,t), \tag{12}$$

defining $\alpha=(4\alpha_1\alpha_2)/(\alpha_1+\alpha_2)$, the $I(n_1,n_2,\alpha_1,\alpha_2,t)$ integral is given by

$$\begin{aligned}&\frac{(2n-1)!!}{2(2\alpha)^n}\sqrt{\frac{\pi}{\alpha}} && \text{if } n_1+n_2+t=2n,\\ &\frac{n!}{2\alpha^{(n+1)}} && \text{if } n_1+n_2+t=2n+1.\end{aligned} \tag{13}$$

Notice that, in this case, the phase factor ($\mathrm{e}^{-\mathrm{i}\mathbf{pA}}$) is a constant and can therefore be neglected since both basis functions are centered on the same atom. However, this phase factor cannot be obviated in the two-center integrals, in which the integral to calculate is

$$\begin{aligned}\left\langle\widehat{\varphi}^{m_1}_{n_1,l_1}|p^t|\widehat{\varphi}^{m_2}_{n_2,l_2}\right\rangle=&(-\mathrm{i})^{l_2}\mathrm{i}^{l_1}\frac{B(n_1,\alpha_1)B(n_2,\alpha_2)}{(2\alpha_1)^{(n_1+1/2)}(2\alpha_2)^{(n_2+1/2)}}\\ &\times\int_0^\infty \mathrm{d}p\,p^{n_1+n_2+t}\,\mathrm{e}^{-p^2/\alpha}\\ &\times\int_\Omega \mathrm{d}\Omega\,Z_{l_1,m_1}(\theta_p,\phi_p)Z_{l_2,m_2}(\theta_p,\phi_p)\mathrm{e}^{-\mathrm{i}\mathbf{p}(\mathbf{A}-\mathbf{B})}\end{aligned} \tag{14}$$

with α defined as above and **A** and **B** are the position vectors of the nucleus where $\widehat{\varphi}^{m_1}_{n_1,l_1}$ and $\widehat{\varphi}^{m_2}_{n_2,l_2}$, respectively, are centered.

Defining $\mathbf{C}=\mathbf{A}-\mathbf{B}$, C as the modulus of **C**, and using the expansion

$$\mathrm{e}^{-\mathrm{i}\mathbf{pC}}=4\pi\left(\frac{\pi}{2pC}\right)^{1/2}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}(-\mathrm{i})^l J_{l+1/2}(pC)Z_{l,m}(\theta_p,\phi_p)Z_{l,m}(\theta_C,\phi_C), \tag{15}$$

Table 1
Bond distances, 6-311$G(d,p)$ and Hartree–Fock-limit energies (in a.u.) for diatomic molecules.

Molecule	R	$E_{6\text{-}311G(d,p)}$	$E_{\text{Hartree–Fock}}$
H_2	1.400	−1.132470	−1.133629[a]
LiH	3.015	−7.985892	−7.987313[b]
BeH	2.538	−15.151633	−15.15312[b]
Li_2	5.051	−14.870189	−14.87152[a]
BH	2.336	−25.127442	−25.13137[b]
CH	2.124	−38.277122	−38.27935[b]
NH	1.961	−54.976043	−54.97806[b]
OH	1.834	−75.410472	−75.42083[b]
B_2	3.005	−49.030360	−49.09088[a]
HF	1.732	−100.046515	−100.07030[b]
LiO	3.184	−82.283741	−82.31114[c]
C_2	2.348	−75.393696	−75.40670[a]
BeO	2.514	−89.432706	−89.45047[c]
LiF	2.955	−106.968731	−106.9904[c]
NaH	3.566	−162.378886	−162.3928[b]
BO	2.275	−99.545655	−99.55550[c]
BeF	2.572	−114.144743	−114.1688[c]
MgH	3.271	−200.149143	−200.1566[b]
N_2	2.068	−108.970124	−108.9928[a]
CO	2.132	−112.768224	−112.7860[c]
BF	2.391	−124.136996	−124.1659[c]
AlH	3.114	−242.455533	−242.4634[b]
NO	2.174	−129.280771	−129.2837[c]
CF	2.402	−137.207945	−137.2169[c]
SiH	2.874	−289.430918	−289.4362[b]
O_2	2.282	−149.656179	−149.6659[a]
NF	2.489	−153.820826	−153.8311[c]
PH	2.708	−341.286703	−341.2932[b]
OF	2.495	−174.172663	−174.19502[d]
SH	2.551	−398.092861	−398.1015[b]
F_2	2.680	−198.726859	−198.7701[a]
HCl	2.408	−460.094904	−460.1103[b]
AlF	3.126	−341.449626	−341.48319[e]
SiO	2.854	−363.815840	−363.8516[e]
PN	2.818	−395.156048	−395.18476[e]

[a] Ref. [11]; [b] ref. [13]; [c] ref. [12]; [d] ref. [34]; [e] ref. [31,32].

where $J_{l+1/2}(pC)$ is a Bessel function of first order and $Z_{l,m}(\theta_C,\phi_C)$ is the real harmonic corresponding to the $\mathbf{C}$ vector, the integral of equation (14) can be written as

$$\left\langle \widehat{\varphi}^{m_1}_{n_1,l_1} \middle| p^t \middle| \widehat{\varphi}^{m_2}_{n_2,l_2} \right\rangle = (-\mathrm{i})^{l_2}\mathrm{i}^{l_1} \frac{B(n_1,\alpha_1)B(n_2,\alpha_2)}{(2\alpha_1)^{(n_1+1/2)}(2\alpha_2)^{(n_2+1/2)}} \left(\frac{\pi}{2C}\right)^{1/2} \times \sum_{l=|l_1-l_2|}^{l_1+l_2(2)} \sum_{m=-l}^{l} \mathrm{i}^l Z_{l,m}(\theta_C,\phi_C) A^{l_1m_1l_2m_2}_{lm} K(n_1,n_2,\alpha,l,t). \tag{16}$$

Table 2

$\langle p^t \rangle$ values for diatomic molecules (in a.u.).

Molecule	$\langle p^{-2} \rangle$	$\langle p^{-1} \rangle$	$\langle p^{0} \rangle$	$\langle p^{1} \rangle$	$\langle p^{2} \rangle$	$\langle p^{3} \rangle$	$\langle p^{4} \rangle$
H_2	6.38377476	3.12393089	2.00000000	1.81851511	2.24458644	3.88375519	10.7275664
LiH	15.0577992	5.66106447	4.00000000	5.89885402	15.9675311	72.4492340	595.451058
BeH	17.8176511	6.60918946	5.00000002	8.58182894	30.2939499	185.152751	2036.70795
Li_2	45.0639587	10.6149272	6.00000000	9.82034235	29.7761377	141.881027	1185.69841
BH	19.0212432	7.02079052	6.00000000	11.6992713	50.2373499	383.769765	5276.27892
CH	13.8708068	6.79380340	7.00000000	15.5371429	76.5406738	690.257091	11337.1834
NH	10.8944759	6.60392941	8.00000000	19.9773754	109.954042	1132.94270	21532.0806
OH	8.99614067	6.48681979	9.00000000	24.9095290	150.848889	1740.79958	37516.3815
B_2	22.1959622	10.4208567	10.0000000	21.6120839	97.6062785	756.634201	10446.8950
HF	7.57189063	6.36705854	10.0000000	30.4430181	200.169767	2543.31667	61135.0706
LiO	11.1455413	8.14360476	11.0000000	29.1135973	164.515537	1807.60522	38069.3776
C_2	19.5408524	10.3665659	12.0000000	29.2320537	150.770788	1377.09309	22677.2125
BeO	12.6921829	8.96621322	12.0000000	31.8849459	178.707830	1917.14781	39463.8335
LiF	9.40085193	7.88142571	12.0000000	34.7338172	214.031653	2610.78737	61693.6907
NaH	20.3300248	9.33275709	12.0000000	41.6803259	324.518900	4884.71494	142555.504
BO	15.6091985	9.91129979	13.0000000	35.0683731	198.917759	2115.02860	42677.3201
BeF	17.9426617	9.69696585	13.0000000	37.2827065	228.316834	2724.17802	63151.0383
MgH	27.5737000	10.6589051	13.0000000	47.5622593	400.064009	6496.25930	205415.955
N_2	16.9265802	10.5921289	14.0000000	38.0685641	217.587880	2261.33146	43049.0966
CO	17.4976273	10.5864471	14.0000000	38.6476352	225.271267	2426.22108	48818.4500
BF	20.6026505	10.7345163	14.0000000	40.2677229	248.242993	2924.56876	66434.9295
AlH	31.3274911	11.3415384	14.0000000	53.7323244	484.822291	8442.32671	287165.005
NO	15.5746787	10.5790119	15.0000000	42.9193868	258.270767	2868.73344	59035.1392
CF	16.7603620	10.6414095	15.0000000	44.0304260	274.424832	3231.37723	72507.7478
SiH	25.6360713	11.3551890	15.0000000	60.2858501	578.813354	10749.8397	391481.284
O_2	14.2566134	10.6272180	16.0000000	47.7201569	299.010669	3478.66893	75078.8865
NF	14.4062532	10.6016340	16.0000000	48.3382793	307.649180	3675.94847	82758.4481
PH	22.4938523	11.4307889	16.0000000	67.1638179	682.547339	13456.7778	521376.690
OF	13.0377881	10.6255543	17.0000000	53.1551410	348.457364	4287.11305	98839.3993
SH	19.6146776	11.4298716	17.0000000	74.3386853	796.151703	16599.6243	682339.413
F_2	12.0263502	10.7108809	18.0000000	58.4190012	397.226313	5093.26311	122608.723
HCl	16.8651564	11.3666975	18.0000000	81.8676518	920.206682	20215.3173	877638.099
AlF	30.3660705	14.6992418	22.0000000	82.4264965	682.906467	10981.7010	348273.880
SiO	25.9959247	14.6968941	22.0000000	83.5084611	727.501249	12483.7605	428895.745
PN	26.1413627	15.1700371	22.0000000	85.2594329	790.051472	14584.5810	524860.751

The $A_{lm}^{l_1m_1l_2m_2}$ factors are related to the Gaunt coefficients [14] and come from the integral

$$A_{lm}^{l_1m_1l_2m_2} = 4\pi \int_\Omega \mathrm{d}\Omega \, Z_{l_1,m_1}(\theta_p,\phi_p) Z_{l_2,m_2}(\theta_p,\phi_p) Z_{l,m}(\theta_p,\phi_p). \tag{17}$$

The evaluation of the integral $K(n_1,n_2,\alpha,l,t)$ in equation (16) is presented in the appendix.

3. Moments of diatomic molecules

Hartree–Fock calculations for the ground state of 35 diatomic molecules at the equilibrium distance were performed with 6-311$G(d,p)$ basis sets [29,30,36,37] using

Gaussian 94 program of Pople et al. [20]. HF energies are given in table 1 and are compared with the energies obtained using Hartree–Fock limit wave functions [11,13,14,20,29,30,36,37]. The 6-311G basis set can be used for all the atoms involved in these molecules, triple zeta valence and double zeta valence are the qualities to p and s functions, respectively. The inclusion of double diffuse functions (d,p) amplifies the above basis set with the Complete Basis Set method of Petersson et al. [29,30,36,37]. The largest energy differences obtained in table 1 appear in B_2 and F_2 molecules. The HF molecular wave functions expanded in the 6-311$G(d,p)$ basis sets are employed to compute the moments, whose values are summarized in table 2. The number of significant figures for $\langle p^t \rangle$ values is limited by the accuracy of the wave function rather than by the algorithms employed in the moment calculations. The exponents for GTOs

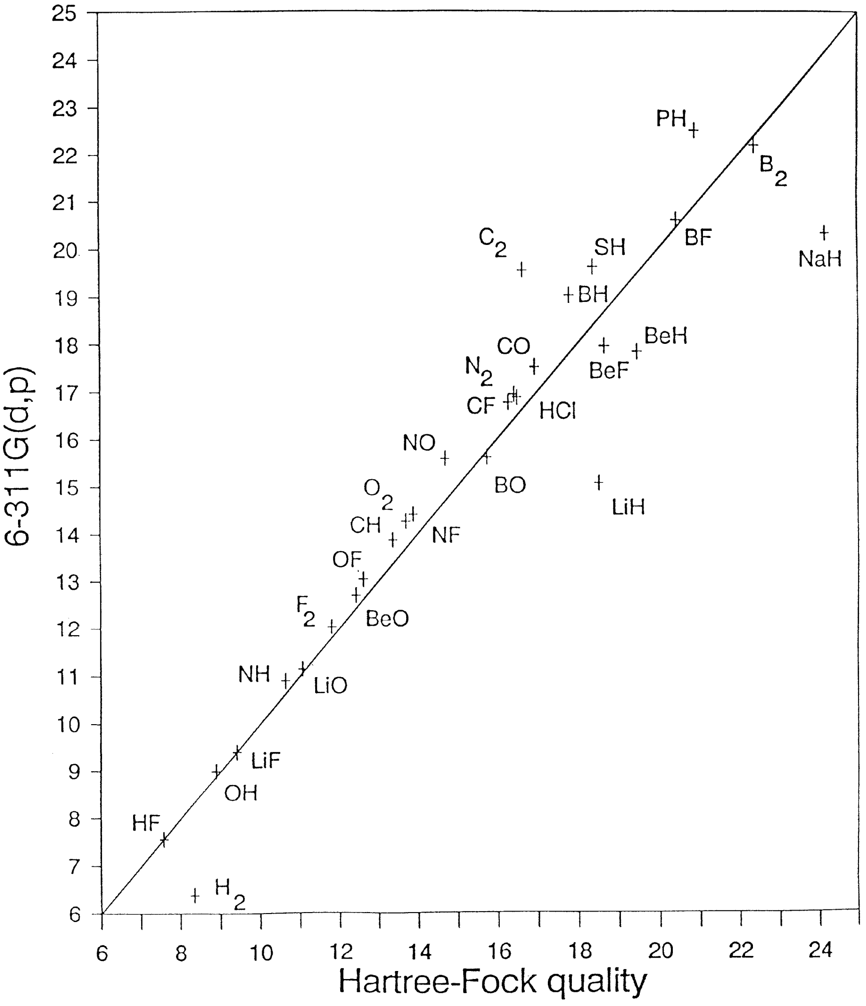

Figure 1. Comparison of present 6-311$G(d,p)$ and Hartree–Fock-limit $\langle p^{-2} \rangle$ (a.u.) in diatomic molecules. The line drawn represents the diagonal.

are obtained with three to eight figures: three figures for the more contracted functions and eight figures for the polarization functions, while the coefficients are obtained with nine significant figures. We have found that the values of table 2 have a precision of nine figures, as observed from the $\langle p^0 \rangle$ values, corresponding to the normalization.

The program developed with the above formulas has been adapted to the output of Gaussian 94 program for open and closed shell diatomic molecules including d functions. Values of $\langle p^t \rangle$ presented in table 2 are close to those of the HF-limit [35], except for the $\langle p^{-2} \rangle$ and $\langle p^4 \rangle$ values. These results are expected because the HF-limit wave functions are expanded in Slater type functions while the present calculations are carried out with GTOs and the inability of GTOs to satisfy the electron-nucleus cusp condition [41] is well known.

Graphic examples of the behaviour of the values of table 2 and the values of

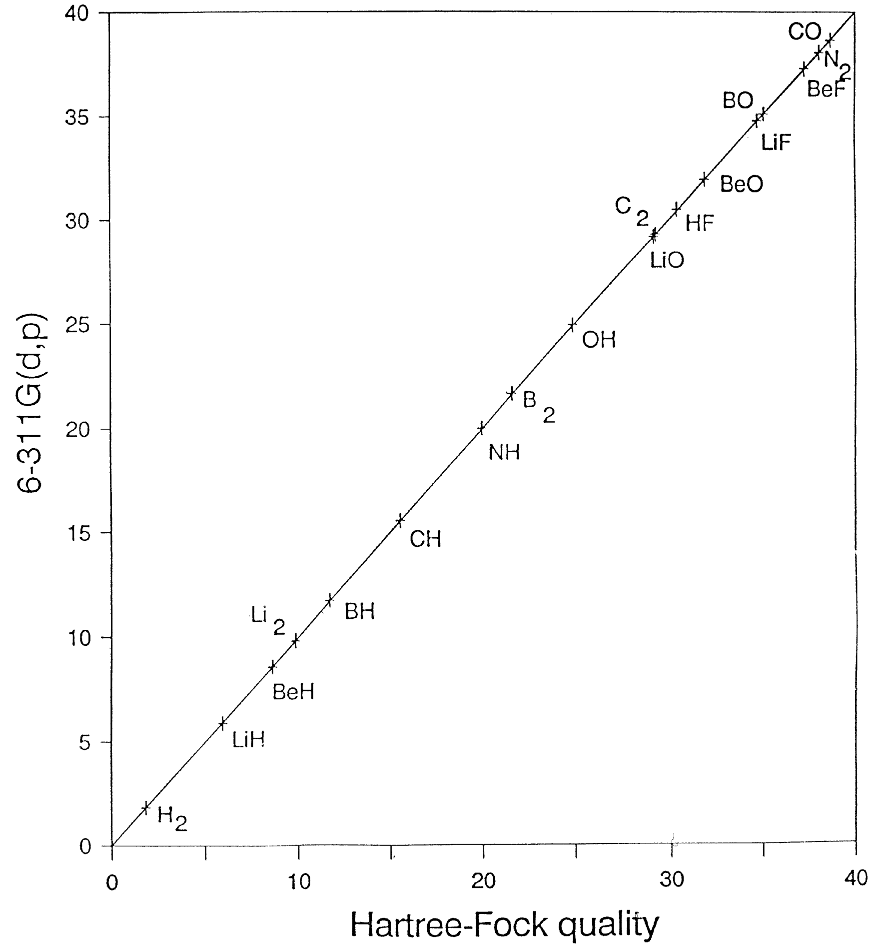

Figure 2. Comparison of present 6-311$G(d,p)$ and Hartree–Fock-limit $\langle p^1 \rangle$ (a.u.) in diatomic molecules. The line drawn represents the diagonal.

HF-limit are depicted in figures 1 and 2, respectively. A comparison of $\langle p^{-2} \rangle$ values for the molecules with up to 25 electrons is presented in figure 1. Molecules above the diagonal show $\langle p^{-2} \rangle$ values which are higher with 6-311$G(d,p)$ basis sets than with HF-limit wave functions. The largest discrepancies are obtained for hydrides, specially alkaline hydrides. The same comparison for the $\langle p^1 \rangle$ is shown in figure 2 for molecules with up to 40 electrons. In this case both sets of values are similar, that is the crosses are on the diagonal.

The results obtained in this paper support the conclusion that the moments $\langle p^t \rangle$ can be calculated from analytic formulae for GTOs without approximations. Using extended GTO basis sets, one can obtain values of HF-limit for powers from $t = -1$ to 3. Larger basis sets are needed for accurate predictions of $\langle p^{-2} \rangle$ and $\langle p^4 \rangle$. These p-space properties have a direct relation with the molecular density properties.

Acknowledgements

This work has been supported by the Dirección General de Investigación Científica y Técnica of Spain (PB94-0160). We thank Prof. J. Fernández Rico and Dr. R. López for their comments.

Appendix

The p integral obtained in the two-center momentum expectation values

$$\int_0^\infty \mathrm{d}p\, p^{n_1+n_2+t-1/2} J_{l+1/2}(pC)\, \mathrm{e}^{-p^2/\alpha}$$

can be solved using the equation (6.631) of [27]. After some index transformation it can be rewritten as

$$K(n_1,n_2,\alpha,l,t) = C^{(l+1/2)} \frac{\Gamma\left(\frac{l+n_1+n_2+l-1}{2}\right)\alpha^{(l+n_1+n_2+t-1)/2}}{2^{(l+3/2)}\Gamma\left(l+\frac{3}{2}\right)} \times {}_1F_1\left(\frac{n_1+n_2+t+l+1}{2}, l+\frac{3}{2}; -\frac{C^2\alpha}{4}\right), \tag{18}$$

${}_1F_1(a,b;z)$ being the degenerate hypergeometric function:

$${}_1F_1(a,b;z) = \sum_{k=0}^{\infty} \frac{(a)_k}{(b)_k k!} z^k. \tag{19}$$

Since GTO functions do not satisfy the cusp condition, the optimization of their exponents with respect to the energy is partially compensated by including very concentrated functions, i.e., with high exponents (normally for $1s$ functions). This fact determines that the argument of the hypergeometric function may take high values while the convergence of series of equation (19) is very slow.

Table 3
Convergence of the asymptotic expansion of equation (21).

n_1	n_2	l	Number of terms in the hypergeometric series			
			$z = -100$	$z = -250$	$z = -500$	$z = -1000$
1	1	0	15	10	8	6
1	2	1	16	10	8	7
2	2	0	17	11	8	7
2	2	2	17	11	8	7
1	3	2	17	11	8	7
2	3	1	19	11	9	7
2	3	3	18	11	9	7
3	3	0	20	12	9	8
3	3	2	20	12	9	7
3	3	4	19	12	9	7

The first step in the calculation of the hypergeometric function is the application of the Kummer's transformation

$$ {}_1F_1(a,b;-z) = \mathrm{e}^{-z}\, {}_1F_1(b-a,b;z). \tag{20}$$

Secondly, the computation of the hypergeometric function has been carried out depending on the value of the third argument. This can be evaluated directly with equation (19) for $z > -100$, and the desired accuracy is achieved. For other arguments which are higher than the considered threshold two cases have been considered:

- if the first argument is either a negative integer or zero, the series is a finite polynomial;
- if this is not the case, the asymptotic expansion [1] is used:

$$\begin{aligned}\frac{{}_1F_1(a,b;z)}{\Gamma(b)} = {}& \frac{\mathrm{e}^{\pm \mathrm{i}\pi a}\, z^{-a}}{\Gamma(b-a)}\left\{\sum_{n=0}^{R-1}\frac{(a)_n(1+a-b)_n}{n!}(-z)^{(-n)} + \mathrm{O}\big(|z|^{-R}\big)\right\}\\ &+\frac{\mathrm{e}^{z}\, z^{a-b}}{\Gamma(a)}\left\{\sum_{n=0}^{S-1}\frac{(b-a)_n(1-a)_n}{n!}(z)^{-n} + \mathrm{O}\big(|z|^{-S}\big)\right\},\end{aligned} \tag{21}$$

  in which the upper sign in the exponential is taken if $-\pi/2 < \arg z < (3\pi)/2$, while the lower sign in the exponential is taken if $-(3\pi)/2 < \arg z \leqslant -\pi/2$.

The convergence behaviour of this series can be studied in table 3. This table summarizes the number of terms needed in the series to increase the accuracy up to 0.5×10^{16} in the hypergeometric value for two functions with n_1 and n_2, with $t = 3$ and several arguments ($z = -100, -250, -500, -1000$). The convergence of this asymptotic expansion is faster as the argument decreases.

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