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A Simple Method to Calculate the Expectation Values of the Linear Momentum Operator p in Molecules

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The proportionality between the expectation values $\langle p^n \rangle$ and the Slater effective parameters to the same power, α^n, have been used with the method of Eisenberger & Marra [*Phys. Rev. Lett.* (1971), **27**, 1413–1416] in order to obtain localized expectation values of the linear momentum operator. A compilation of $\langle p^2 \rangle/2$ and of $\langle p^{-1} \rangle/2$ is presented for a set of AB and AH bonds, H is the hydrogen atom, while A and B vary from lithium to fluorine. A correction introducing the internuclear distances R_{AB} is proposed, which increases the accuracy of the results. For a given molecule it is sufficient to sum the bond terms with or without the R correction, using the Lewis localization technique. This method is useful for large molecules.

Introduction

In recent years, a large amount of work has been done on the Compton scattering produced by X-rays, γ-rays and fast electrons. The theoretical work depends directly on knowledge of the wave function of the scatterer. For the present state of experimental and theoretical results see Williams (1977), in which the references alphabetically listed from Eisenberger & Platzman (1970) to Whangbo, Smith & Von Niessen (1974) and the review article by Epstein (1973*a*) are included.

An algebraic method is proposed to calculate the expectation values of the linear momentum operator in the form of localized values in order to see if these are transferable; they can be useful for large molecules when there are no wave functions.

In this article, the starting points are the $\langle p^n \rangle$ values calculated from the BAS (best atomic set) and RHF (restricted Hartree–Fock) wave functions, particularly those calculated by Ransil, (1960), Cade & Huo (1973, 1975), Cade & Wahl (1974), Moccia (1964*a*,*b*,*c*), Epstein (1970, 1973*b*), Whangbo, Smith & Von Niessen (1974), Smith & Whangbo (1974), Alhenius & Lindner (1975) and Kaijser & Lindner (1975).

Method of calculation

The usual way of calculating the expectation values of the linear momentum operator $\langle p^n \rangle$ is to start from the wave function in position space which by Fourier transformation gives the corresponding wave function in momentum space

$$\chi(\mathbf{p}) = (2\pi)^{-3/2} \int \psi(\mathbf{r}) \exp(-i\mathbf{p}.\mathbf{r}) \mathrm{d}\mathbf{r} \tag{1}$$

where $\psi(\mathbf{r})$ is the usual Slater-type orbital

$$\psi(\mathbf{r}) = N^{1/2} r^{n'-1} \exp(-\alpha r) Y_{l,m}(\theta, \psi). \tag{2}$$

In the impulse approximation and for an isotropic system the expectation values take the form

$$\langle p^n \rangle = \int I(p) p^n \mathrm{d}p, \tag{3}$$

where $I(p)$ the radial momentum density is

$$I(p) = \int \chi^x(\mathbf{p}) \chi(\mathbf{p}) p^2 \sin\theta_p \mathrm{d}\theta_p \mathrm{d}\varphi_p, \tag{4}$$

the Compton profile is

$$J(q) = \tfrac{1}{2} \int_q p^{-1} I(p) \mathrm{d}p \tag{5}$$

with

$$q = \frac{cl}{2\lambda_i \sin} \theta/2, \tag{6}$$

c is the velocity of the light, λ_i is the wavelength of the incident beam, l is measured from the centre of the Compton profile and θ is the scattering angle. It also appears that

$$\langle p^{-1} \rangle = 2J(0). \tag{7}$$

For these relations see Eisenberger & Platzman (1970) and Kilby (1965).

The results obtained by this procedure will be compared with those of the proposed method. This method is an extension of the proportionality between the $\langle p^n \rangle$ values and the effective parameters of the Slater-type orbital, of the form given by (2), which has been demonstrated by Epstein & Roux (1974) in the case of atoms as

$$\frac{\langle p^n \rangle}{\alpha^n} = C_{n,n'l,m}, \tag{8}$$

where C is nearly constant and n', l, m are the usual quantum numbers.

Table 1. *Comparison of kinetic energies (atomic units)*

Molecule	BAS'_2	BAS'_1	BAS	RHF'_2	RHF'_1	RHF
NO	128·247	128·250		129·060	129·073	129·146
BF	123·186	123·542	123·164	123·263	123·712	124·116
CO	111·777	111·948	111·352	112·337	112·543	112·642
NF	153·118	153·198		153·306	153·415	153·831
HCN	91·363	91·733	91·327	92·610	92·562	92·836
FCN	189·838	190·412		190·903	191·083	191·627 $(-E)$
NNO	181·553	181·561	181·560	183·389	183·408	183·563 $(-E)$
FCCH	17·472	174·725		174·910	174·951	175·616 $(-E)$
NCCCH	166·369	166·741		168·269	167·962	168·487 $(-E)$

Notes

BAS'_2: BAS approximation with equation (10).
BAS'_1: BAS approximation with equation (9).
BAS: BAS approximation, direct calculations (Epstein, unpublished results).
RHF'_2: RHF approximation with equation (10).
RHF'_1: RHF approximation with equation (9).
RHF: RHF approximation, direct calculations with wave functions from Cade & Wahl (1974), Cade & Huo (1973, 1975) and Yoshimine & McLean (1967).
$(-E)$ indicates the use of Virial theorem to obtain the kinetic energies.

In the case of bonds, two relations have been proposed in order to converge to the atomic value when the internuclear distance R becomes zero:

$$\frac{\langle p^n \rangle}{\alpha^n + \beta^n} = F_1(S,S',S''\ldots) \tag{9}$$

and

$$\frac{\langle p^n \rangle}{(\alpha + \beta)^n} = F_2(S,S',S''\ldots). \tag{10}$$

Whatever the wave functions used to calculate the $\langle p^n \rangle$ values of the numerators of these two equations, the values of the denominators remain the same Slater atomic parameters: α is the STO centred on atom A, β on atom B. They are the same as those used by Ransil (1960). The Eisenberger & Marra (1971) method is then applied to calculate the $\langle p^n \rangle$ for (9) and (10). Their method requires the total $\langle p^n \rangle_T$ calculated from wave functions of various accuracies from which the 1*s* atomic or inner-shell contributions are subtracted. The remaining parts, $\langle p^n \rangle_R$, can be divided between the bond and lone-pair contributions. This can be done with the following system of equations:

$$\begin{aligned} \langle p_1^n \rangle R' &= a\langle p^n \rangle_{\mathrm{LP}A} + b\langle p^n \rangle_{\mathrm{LP}B} + c\langle p^n \rangle_{AB} \\ \langle p_2^n \rangle R' &= a'\langle p^n \rangle_{\mathrm{LP}A} + b'\langle p^n \rangle_{\mathrm{LP}B} + c'\langle p^n \rangle_{AB} \\ \langle p_2^n \rangle R' &= a''\langle p^n \rangle_{\mathrm{LP}A} + b''\langle p^n \rangle_{\mathrm{LP}B} + c''\langle p^n \rangle_{AB}; \end{aligned} \tag{11}$$

the $\langle p_M^n \rangle_{R'}$ are the $\langle p^n \rangle_{R'}$ of molecules 1, 2, 3; a, a', a'', b, b', b'', are the number of lone pairs on A and B atoms, respectively; c, c', c'', the number of bonds between A and B; $\langle p^n \rangle_{\mathrm{LP}A,\,\mathrm{LP}B}$ the $\langle p^n \rangle$ value for the AB bond.

The F_1 and F_2 functions vary with the types of atoms which form the bond, therefore they are also functions of the nuclear charges. As in the case of atoms, straight lines are good approximations of F_1 and F_2 functions plotted *versus* $(Z_A + Z_B)$, so only two values are necessary for each value of n and each type of bond and lone pair.

Results and discussion

Examples of kinetic energies and $\langle p^{-1} \rangle$ values obtained by the proposed method are collected in Tables 1 and 2 and compared with the results obtained by direct calculations. It can be seen that in the case of the kinetic energies, we can get a good approximation to the direct results with the use of the RHF'_1 method (use has been made in some cases of the Virial theorem to obtain the kinetic energies). In the case of the $\langle p^{-1} \rangle$ values, the results suggest the use of the BAS'_1 approximation.

The results show a crude character of transferability but they are strongly influenced by several factors, particularly by the choice of 1*s* contributions and the internuclear distances. Alhenius & Lindner (1975) have discussed these two effects in the case of the kinetic energies; in the case of $\langle p^{-1} \rangle$, the effect of the 1*s* contribution is very important as it is used in the comparison of the theoretical and experimental values. The $\langle p^{-1} \rangle$ are also largely modified by the internuclear distance. This effect has been treated as follows: As was shown by Eisenberger & Marra (1971) the $\langle p^n \rangle_{AB}$ are inversely proportional to the internuclear distances R_{AB}, particularly

$$\frac{\langle p^2 \rangle_{c-c}}{2} > \frac{\langle p^2 \rangle_{c=c}}{2}$$

this implies that

$$\frac{\langle p^{-1} \rangle_{c-c}}{2} < \frac{\langle p^{-2} \rangle_{c=c}}{2}$$

Table 2. *Comparison of* $\langle p^{-1}\rangle_T/2$ *values (atomic units)*

Molecule	BAS_2'	BAS_1'	BAS	RHF_2'	RHF_1'	RHF	CI	DZ	EXP
CH	3·16	3·16		3·38	3·39	3·4393367		3·46 (1)	
FH	3·12	3·13	3·1488	3·23	3·22	3·234261		3·19 (2)	
C_2	5·29	5·24	5·2016	5·39	5·34				
CO	5·08	5·14	5·1482	5·29	5·35	5·321130	5·16	5·17 (3)	
NF	5·14	5·15		5·40	5·42		5·09		
BF	4·98	5·10	5·1604	5·20	5·32	5·416703			
N_2			5·1312			5·344320	4·97		5·27
CH_4	5·08	5·09	5·036	5·70	5·66			5·08 (4)	4·985

Notes

BAS_2', BAS_1', BAS, RHF_2', RHF_1', RHF, have the same meaning as in Table 1.

CI: valence electron configuration interaction wave function results (Kaijser & Lindner, 1975).

DZ: double zeta wave function results (Whangbo, Smith, & Von Niessen, 1974).

EXP: experimental values, Eisenberger & Reed (1972) for N_2, and Whangbo, Smith & Von Niessen (1974) for CH_4.

Table 3. *Influence of the choice of* 1*s contribution and* R_{AB} *upon* $\langle p^{-1}\rangle_T/2$ *(atomic units)*

	BAS_1'	BAS_2'	RHF_1' 1,4-Dioxane	RHF_2'	LMO E	LMO S & W	EXP
CMO 1*s*	20·67	20·59	22·02	22·08			
LMO 1*s*	20·52	20·42	21·85	21·79	19·59	19·73	19·39
R corrected and							
CMO 1*s*	19·41	19·33	20·72	20·67			
LMO 1*s*	19·23	19·16	20·54	20·50	19·59	19·73	19·39
			Hexane				
CMO 1*s*	24·66	27·78	26·48	26·86			
LMO 1*s*	24·42	24·60	26·30	26·57	23·74	23·23	22·34 22·84
R corrected and							
CMO 1*s*	23·50	23·58	25·32	25·66			
LMO 1*s*	23·31	23·40	25·16	25·48	23·74	23·23	22·34 22·84

Notes

BAS_1', BAS_2', RHF_1', RHF_2', have the same meaning as in Tables 1 and 2.

LMO E: localized molecular orbital values (Epstein, 1970).

LMO S & W: localized molecular orbitals (Smith & Whangbo, 1974).

CMO 1*s*: canonical 1*s* contribution (the canonical orbitals have the property of being eigenfunctions of the Fock operator).

LMO 1*s*: localized canonical orbital 1*s* contributions.

R corrected: value multiplied by the ratio of internuclear distances.

EXP: experimental values deduced from various authors (Williams, 1977).

Table 4. *Influence of R correction on the kinetic energies (atomic units)*

Molecule	RHF_1'	RHF_1' *R* corrected	Direct calculation	
C_2H_4	77·458	77·906	78·015	$(-E)$
C_2H_6	78·4711	79·149	79·204	$(-E)$
NC_3H	167·96	168·000	168·4868	$(-E)$

Notes

RHF_1': RHF approximation with equation (9).

RHF_1': *R* corrected: RHF_1' values multiplied by the ratio of internuclear distances.

Direct calculation: RHF direct calculation of kinetic energies with the Virial theorem.

We have applied these crude corrections, by multiplying the obtained expectation values by the correct ratio of the internuclear distances. The results are given in Table 3 as well as the 1*s* contribution for the case of $\langle p^{-1}\rangle_T/2$, and in the case of kinetic energies in Table 4 they are compared for the first two molecules with the direct calculations of Smith & Whangbo (1974) with the DZ approximation and for the third molecule with the calculations of Yoshimine & McLean (1967) with the near-Fock approximation.

It is evident that the *R* correction increases the accuracy of the calculated values. From all these results we suggest the use of the values $\langle p^{-1}\rangle_{AB}/2$ and $\langle p^2\rangle_{AB}/2$ taken from Table 5 with or without *R* correction.

Table 5. $\langle p^{-1}\rangle_{AB}/2$, $\langle p^{2}\rangle_{AB}/2$ *and* R_{AB} *(atomic units)*

All quantities are given for one electron and for the indicated internuclear distances.

Bond		$\langle p^{-1}\rangle_{AB}/2$		$\langle p^{2}\rangle_{AB}/2$	R_{AB}
LiH				0·410	3·015
BeH				0·537	2·538
BH		0·704		0·719	2·336
CH		0·599		0·959	2·124
NH		0·518		1·2649	1·9614
OH		0·453		1·6356	1·8321
FH		0·404		2·0825	1·7328
LiLi		1·9075		0·2391	5·051
BeBe		1·182		0·5275	4·000
BB		0·830		0·9190	3·005
CC		0·606		1·4048	2·3481
NN		0·459		2·0190	2·068
OO		0·345		2·6732	2·2820
FF		0·272		3·4205	2·6800
BF		0·515		2·2223	2·3910
CN		0·530		1·7041	2·2140
CO		0·471		2·0556	2·1320
CF		0·425		2·441	2·402
NO		0·406		2·3343	2·1747
NF		0·351		2·7251	2·4890
Lone pair					
B		0·686		0·933	
C		0·553		1·4365	
N		0·466		2·040	
O		0·404		2·7439	
F		0·356		3·5152	
1*s*	BAS	CMO	LMO		
Li	0·3255	0·3266	0·2986	3·6097	
Be	0·2345	0·2378	0·2150	6·78595	
B	0·1848	0·1830	0·1676	10·926130	
C	0·1523	0·1537	0·1373	16·04189	
N	0·1295	0·1305	0·1154	22·12790	
O	0·1130	0·1135	0·991	29·19514	
F	0·097	0·1005	0·0869	37·22895	

Notes

CMO 1*s*: canonical 1*s* contribution as in Table 3.

LMO 1*s*: the corresponding localized values as in Table 3.

BAS are the 1*s* contribution obtained by Epstein (1970).

Conclusion

Despite the simplicity of the method, we obtain satisfactory results assuming a complete transferability of the localized values and improved results using the corrected transferability, although there are still differences to be corrected. A particular advantage of the method is the possibility of starting with $\langle p^n\rangle_T$ derived from very elaborate wave functions. Unfortunately, wave functions of high accuracy are not numerous and it is difficult to obtain homogeneous starting values.

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