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Comment on Momentum Distributions of Valence Electrons of Atoms and Simple Molecules

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Synopsis. The relationship between vertical ionization potentials and experimental electron momentum distributions of individual valence orbitals has been examined in some series of orbitals with the same characteristics of atoms and simple molecules. It has been found that effectively pure s- and p-orbitals show trends consistent with the predicitions of the virial theorem.

The symmetric noncoplanar configuration of the binary (e,2e) method is powerful for studies of molecular electronic structure. This technique provides not only binding energy spectra of valence electrons of atoms and molecules but also their orbital momentum distributions (MD).[1—20] The relative (e,2e) cross-section is essentially given by the square of the Fourier transform of the wave function of the struck electron, in the plane wave impulse approximation including the target Hartree-Fock state.[1—3]

$$\sigma(\mathrm{q}) \propto \left| \int \psi(r) \times \mathrm{e}^{\mathrm{i}\mathrm{q}r} d^3r \right|^2 .$$

In this expression ψ means the one-electron wave function describing the orbital of the struck electron prior to the (e,2e) reaction.

Most of the MD measured so far can be classified into s-type and p-type.[1—20] The former is for orbitals with isotropic spatial distributions, *e.g.*, atomic s-orbitals. The s-type MD shows a maximum at $q=0\ \mathrm{a}_\mathrm{o}^{-1}$. The latter (*i.e.*, p-type) is for those with antisymmetric spatial distributions, *e.g.*, atomic p-orbitals. The p-type MD shows zero intensity at $q=0\ \mathrm{a}_\mathrm{o}^{-1}$ and exhibits a maximum at $q \cong 0.4$—$1.0\ \mathrm{a}_\mathrm{o}^{-1}$.

The virial theorem predicts a relationship between total energy of a molecule and total kinetic energy of the bound electrons. This theorem does not apply to individual orbitals, but some relationship may exist between orbital energy and the kinetic energy of its orbital electron in a series of orbitals with similar characteristics.[21,22] It is interesting to examine the qualitative applicability of the virial theorem to individual orbitals. For this purpose the MD's observed by the binary (e,2e) method can be used as a measure of the kinetic energy of the orbital electron.

The aim of the present study is to discuss and to clarify the relationship between the measured MD and the orbital energy. The MD data used here are those for valence orbitals of rare gas atoms and of molecules which consist of one or two central atoms with or without a few hydrogen atoms: Ne, Ar, Kr, Xe (atoms), HF, HCl, HBr, HI, H_2O, NH_3, CH_4, H_2S, PH_3 (pseudo-atoms), N_2, CO, O_2, (diatomic molecules), and C_2H_2, C_2H_4, C_2H_6 (pseudo-diatomic molecules).[1—20]

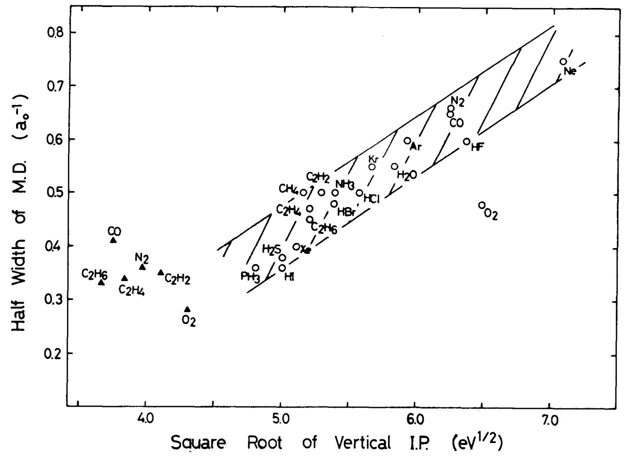

Fig. 1. Correlation between half width (q_hw) of s-type momentum distributions and vertical ionization potentials (IP) for valence orbitals. See text for definition of q_hw and for data marks (○ and ▲). The chemical formula of atoms and molecules are added to the data marks but the orbitals' symbols are omitted for clarity.

Figure 1 shows the degree of correlation between q_hw and the square root of the vertical ionization potential (IP). The q_hw means the momentum at which the s-type MD becomes a half of its maximum intensity. The vertical IP means the centroid of main and all satellite peaks belonging to the same hole state, if satellite peaks are observed in the ionizing process.[1,2] In this case accuracy of the IP is ±1—2 eV. This centroid IP corresponds to the orbital energy when the ground state of the target atom or molecule is well described with a single configuration.[1,2] The open circles (○) indicate the data for the orbitals mainly composed of atomic 2s, 3s, 4s, and 5s-orbitals.[1—20] The solid triangles (▲) indicate the data for the orbitals mainly consisting of bonding combination of atomic 2p-orbitals.[13—20] The error in the estimation of q_hw is about five times the sizes of the circles or triangles shown.

The data shown with the open circles represent a linear relationship between the q_hw and the square root of the vertical IP. This feature means that a high q_hw corresponds to a high IP (a large negative orbital energy in Koopmans' theorem). Thus, the orbital showing a higher q_hw has a spatial distribution which tends to be contracted to regions of larger potential energy, *i.e.*, nearer to the nuclei. The orbital with a lower q_hw is distributed more in regions of lower potential energy. This fact shows that the virial theorem qualitatively holds for individual orbitals at least in the series of the orbitals studied here which have the s-type MD and consist mainly of atomic s-orbitals. An exception is $O_2 2\sigma_g$ orbital. This is probably due to correlation effects in the neutral ground state as well as in the ionic state.

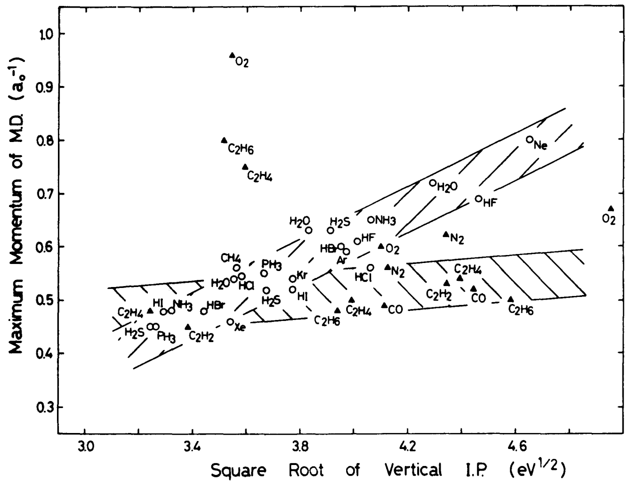

Fig. 2. Correlation between maximum momentum (q_m) of p-type momentum distributions and vertical ionization potentials (IP) for valence orbitals. See text for definition of q_m and for data marks (○ and ▲).

The relation between the solid triangles' data and the IP is complicated. The virial theorem can not be applied to this type of the orbitals.

Figure 2 shows correlation between q_m and the square root of the vertical IP. The q_m indicates the momentum at which the p-type MD is a maximum. The open circles (○) are data for the orbitals of the atoms and the pseudo-atoms. The solid triangles (▲) are data for the orbitals of the diatomic and pseudo-diatomic molecules. The errors in estimation of q_m are about four times the sizes of the circles or the triangles shown.

From Fig. 2, it is seen that the q_m for the atoms and the pseudo-atoms has nearly a linear dependence on the square root of the vertical IP. One of the open circles (datum for HCl 5σ orbital) is slightly lower than the hatched area for the atoms and the pseudo-atoms' data. However, the datum point marginally overlaps with the area if the error of q_m is taken into account. This near linear dependence suggests that the virial theorem can qualitatively be applied to individual orbitals in the series of the orbitals of the atoms and the pseudo-atoms showing the p-type MD's which have been examined in the present study.

The orbitals of the diatomic and pseudo-diatomic molecules showing p-type MD's are classified into two groups, antibonding orbitals and others. The former have two nodal planes bisecting the molecular axis and parallel to the axis. Then their wave functions rapidly vary in coordinate space, and the antibonding orbitals are expected to have considerably higher MD's. These orbitals here considered are O_2 1π_g, C_2H_4 1b_{1g} and C_2H_6 1e_g orbitals; q_m=0.96, 0.75, and 0.8 a_o^{-1}, respectively. The three data points of interest are plotted quite high above the hatched area for the atoms and the pseudo-atoms' data.

The second group of the orbital consist of the antibonding combination of atomic 2s-orbitals and π-bonding orbitals. Both have one nodal plane, bisecting the molecular axis or parallel to this axis. The q_m for these orbitals is slightly dependent on the IP. The π-bonding orbital is diffuse and has much weight of spatial distribution in the intermediate region of atoms. The orbitals of 2s antibonding combination is spatially distributed to the opposite regions to the molecular center. These characteristics are assumed to bring about the weak dependent feature of the q_m on the IP. The three data, O_2, 2σ_u, O_2 1π_u, and N_2 2σ_u orbitals, deviate slightly to higher q_m from the hatched area for this group of the orbitals.

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