

COMPTON PROFILE ANISOTROPIES IN DIATOMIC
MOLECULES AND SOLIDS

A Dissertation
Presented to
the Faculty of the Department of Physics
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Bayani Ilas Ramirez

July 1976

ACKNOWLEDGEMENTS

The author expresses his gratitude and thanks to the following: the International Institute of Education (I.I.E.) for a Fulbright-Hays travel grant that enabled him to come to this country from the Philippines, the Physics Department of the University of Houston for providing teaching or research fellowships throughout his graduate career, Dr. Matcha for his willingness to "step" into momentum space, and most importantly, his adviser, Dr. McIntire for suggesting the problem and helping in solving it.

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ABSTRACT

A theoretical calculation of Compton profiles and Compton profile anisotropies in a diatomic molecule using LCAO-MO-SCF (near-Hartree Fock) wavefunctions is presented. The different occupied molecular orbitals (MO) give interesting profiles and anisotropies which are indicative of their roles in the binding of the molecule. The results for the diatomic molecule are extended to approximate a face-centered-cubic (FCC) diatomic crystal using a molecular simulated crystal (MSC) procedure in which the outermost MO's are modified to match the symmetry of the crystalline environment. The resulting Compton profiles are called Symmetry Resolved Profiles (SRP).

This formalism is applied in detail to lithium fluoride (LiF) at an internuclear separation of 3.55 a.u., approximately the crystalline spacing. The results compare favorably with previous anisotropy calculations and experiment. The next crystal studied is lithium hydride (LiH). There is fair agreement between theory and experiment. There are no other reported theoretical calculations for LiH. Results for a number of alkali halides are then presented and trends in the anisotropies in relation to the ionic or covalent character of the molecules are indicated. Spherically-averaged total Compton profiles are also compared with experiments on polycrystalline (isotropic) samples. Good agreement is found in each case considered.

TABLE OF CONTENTS

	PAGE
Acknowledgements	i
Abstract	ii
Table of Contents	iii
List of Figures	iv
List of Tables	v
I. INTRODUCTION AND SURVEY	1
A. Compton Scattering Theory	2
B. Compton Profile Anisotropy	6
C. Previous Calculations	8
II. THEORY	10
III. APPLICATION TO LITHIUM FLUORIDE	24
A. Molecular Compton Profile Anisotropies	24
B. Crystalline Compton Profiles	30
C. Comparison with Experiment	38
IV. APPLICATION TO LITHIUM HYDRIDE	44
A. Molecular Anisotropies	45
B. Molecular Simulated LiH Crystal	48
V. APPLICATION TO OTHER ALKALI HALIDES	58
A. Molecular Anisotropies	58
B. Crystalline Anisotropies	63
C. Total Compton Profiles	70
VI. CONCLUSION	74
APPENDIX A: GAUSS-LEGENDRE QUADRATURE	76
APPENDIX B: MOMENTUM TRANSFORM OF A 3d STO	78
APPENDIX C: OVERLAP TERM IN THE MOMENTUM DENSITY	80
APPENDIX D: COMPUTER PROGRAMS	82
REFERENCES	91

LIST OF FIGURES

FIGURE		PAGE
1	Schematic of Compton Scattering	5
2	Momentum Coordinates Transformation	15
3	FCC Geometry for MSC	22
4	LiF Compton Profile Parallel to the Bond	26
5	LiF Compton Profile Normal to the Bond	28
6	$J_{100}-J_{110}$ Per MO for LiF	33
7	$J_{100}-J_{111}$ Per MO for LiF	35
8	Total $J_{100}-J_{110}$ for LiF: Theory and Experiment	40
9	Total $J_{100}-J_{111}$ for LiF: Theory and Experiment	42
10	J_0-J_{90} for LiH and LiF	47
11	$J_{100}-J_{110}$ for LiH: Theory and Experiment	51
12	$J_{100}-J_{111}$ for LiH: Theory and Experiment	53
13	Compton Profile of LiH	56
14	J_0-J_{90} for Alkali Halides	61
15	$J_{100}-J_{110}$ for Alkali Halides	65
16	$J_{100}-J_{111}$ for Alkali Halides	68
17	Compton Profiles of Alkali Halides	72

LIST OF TABLES

TABLE		PAGE
1	Position and Momentum STO's	18
2	Contribution of Each MO to the $J_{100}-J_{110}$ Anisotropy in LiF	34
3	Contribution of Each MO to the $J_{100}-J_{111}$ Anisotropy in LiF	37
4	MSC-SRP Theoretical Results for LiF	43
5	Characteristics of the Alkali Halides Analyzed by MSC-SRP	59
6	MSC-SRP Results for $J_{100}-J_{110}$ Anisotropy of the Alkali Halides	66
7	MSC-SRP Results for $J_{100}-J_{111}$ Anisotropy of the Alkali Halides	69

I. INTRODUCTION AND SURVEY

Compton profile measurement⁽¹⁻⁴⁾ as a method of probing the electronic structure of atoms, molecules, and solids has experienced rapid development in the past decade after a period of inactivity extending from the 1920's (the year Compton scattering⁽⁵⁾ was introduced) until the 1960's. The recent revival of interest in Compton scattering may be largely attributed to the introduction of γ -ray sources and solid-state detectors which improved the acquisition of experimental data tremendously, and the availability of highly accurate wavefunctions for atoms, molecules, and solids which facilitated the rapid calculation⁽⁶⁾ of theoretical Compton profiles. In particular, the measurement and interpretation of Compton profile anisotropies⁽⁷⁾ has emerged as a very important probe of the electronic structure of solids. Some theoretical calculations of anisotropies have been made.⁽⁷⁻⁹⁾ The more successful of these have utilized either the tight-binding approximation or the free-electron (OPW) approach. In neither case have results been readily identifiable with localized orbitals or bonds.

We have developed a new method for calculating and analyzing Compton profile anisotropies in crystals. Our approach is based on the assumption that the charge distribution in a diatomic molecule in the gas phase is similar to that in the solid; thus, we model the crystal by a suitable orientation of noninteracting diatomic molecules with appropriate symmetry modifications due to the crystalline

environment. Self-consistent-field Hartree-Fock (LCAO-MO-SCF) diatomic wavefunctions are then used to calculate the anisotropies. We refer to this as a Molecular Simulated Crystal (MSC) procedure.

An application of this new procedure to LiF is presented in detail. Contributions of individual molecular orbitals to the anisotropies are analyzed and related to polarization and binding effects in the molecule and crystal. Even for nearly ionic molecules such as LiF, there is some covalent character in the bond, this character is evident in the calculated anisotropies. The computed crystal anisotropies are found to agree satisfactorily with experiment. We then present the results for LiH and other alkali halide molecules and crystals.

A. Compton Scattering Theory

Before we discuss the MSC theory we shall describe briefly what Compton scattering is all about and show how the concept of the Compton profile arises naturally in Compton scattering.

CLASSICAL PICTURE

Compton scattering ⁽¹⁰⁾ is the scattering of a photon by an electron. Imagine a photon of initial 4-momentum $\tilde{k}_i = (\hbar \vec{k}_i, \hbar \omega_i)$ interacting with an electron with initial 4-momentum $\tilde{p}_i = (\vec{p}_i, E_i)$ where $\hbar \vec{k}_i$ and $\vec{p}_i$ are the initial linear momenta of the photon and electron respectively, and $\hbar \omega_i$ and E_i are their respective initial total energies.

If we let $\tilde{k}_2$ and $\tilde{p}_2$ be the corresponding final 4-momenta after the interaction then the scattering process may be described by a single equation in the classical theory. This is known as the conservation of 4-momentum equation given by

$$\tilde{p}_1 + \tilde{k}_1 = \tilde{p}_2 + \tilde{k}_2 \quad (\text{I-1})$$

This equation is equivalent to the conservation of momentum and energy equations in the non-covariant formulation of the problem.

In either formulation the change in wavelength of the scattered photon may be easily derived and yields in the non-relativistic limit⁽¹⁾

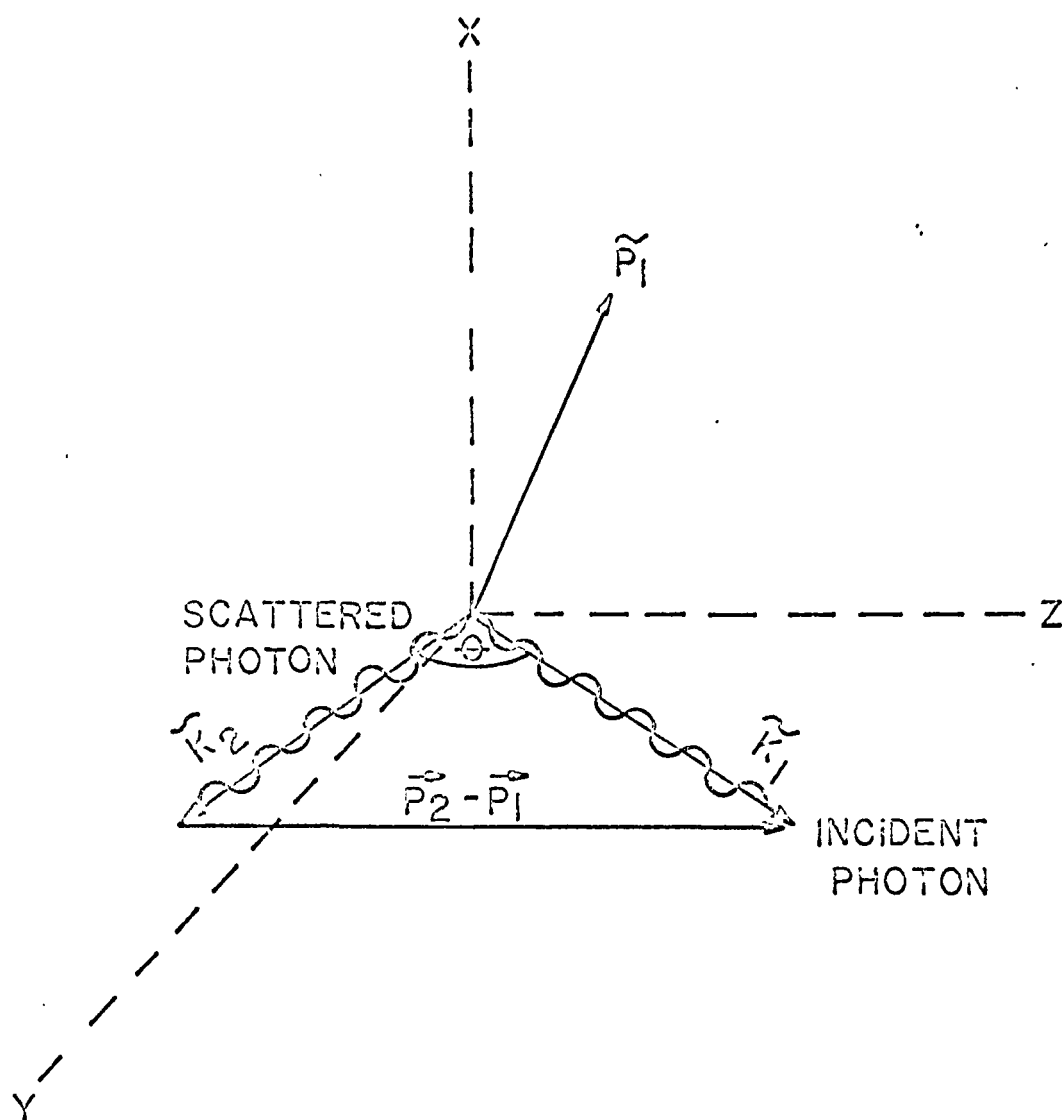
$$\Delta\lambda = \frac{2h}{mc} \sin^2 \frac{\theta}{2} - \frac{2\lambda \sin \theta/2}{mc} p_z \quad (\text{I-2})$$

where h is Planck's constant, m is the mass of the electron, λ is the initial wavelength of the photon, c is the speed of light, θ is the angle between the initial and final directions of the photon, and p_z is the component of the electron's initial momentum along the momentum transfer direction which is chosen as the z -axis (see Figure 1).

The first term in equation (I-1) is the usual Compton wavelength shift obtained if the initial electron is assumed to be at rest. The second term may then be interpreted as a "Doppler shift" effect resulting from the electron's motion

FIGURE 1

Schematic of Compton Scattering.
The momentum transfer direction,
 $\vec{P}_2 - \vec{P}_1$, is shown parallel to the
z-direction.



parallel to the momentum transfer direction. If photons are then scattered off a material where the electrons are performing all kinds of motion, the distribution of the final photons scattered at some angle θ should be an excellent measure of the initial electronic momentum distribution in the material.

QUANTUM PICTURE

Since we are dealing with a process outside of the classical domain of physics, Compton scattering has to be formulated quantum-mechanically. This involves solving Schroedinger's equation (in the non-relativistic limit) and finding the cross-section for photon-electron scattering. In the more general case the electron will be relativistic. The final expression for the differential cross-section relevant to this discussion is given by (1-3)

$$\frac{d\sigma}{d\Omega d\omega_2} = C(\omega_1, \omega_2, p_z, \theta) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(\vec{p}) dp_x dp_y \quad (\text{I-3})$$

where the function C is given by (2)

$$C(\omega_1, \omega_2, p_z, \theta) = \left(\frac{e}{2\pi mc} \right)^4 \frac{\omega_2}{\omega_1} \frac{mc}{(\omega_1^2 + \omega_2^2 - 2\omega_1\omega_2 \cos\theta)^{1/2}} \quad (\text{I-4})$$

in the non-relativistic limit and the so-called impulse approximation.

B. Compton Profile Anisotropy

It is the double integral in equation (I-3) that has been defined as the Compton profile,⁽⁶⁾ i.e.,

$$J(p_z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(\vec{p}) dp_x dp_y \quad (\text{I-5})$$

where ρ is the electronic density distribution in momentum space and where the integration is done on an infinite plane intersecting ρ at some p_z . A Compton profile is therefore a one-dimensional electronic density distribution in momentum space. It also follows that for a single electron the Compton profile satisfies the normalization condition

$$\int_{-\infty}^{\infty} J(p_z) dp_z = 1 \quad (\text{I-6})$$

From equation (I-3) we observe that the Compton profile is directly obtainable from an experimental measurement of the scattered radiation, i.e.,

$$J(p_z) = \frac{d\sigma}{d\Omega d\omega_2} / C(\omega_1, \omega_2, p_z, \theta) \quad (\text{I-7})$$

One of course has to make all the necessary corrections (2-4) present in any experiment before equation (I-5) is applied.

If the electronic density distribution is not spherically-symmetric we should expect the measured Compton profile to vary as the orientation of the material with respect to the initial radiation is changed. We may then define a Compton profile anisotropy (7) as the difference between two Compton profiles associated with two different

scattering directions, i.e.,

$$\Delta J(\rho_z) = J_1(\rho_z) - J_2(\rho_z) \quad (\text{I-8})$$

This Compton profile anisotropy is a very important quantity in the field of Compton scattering since it contains a wealth of information regarding the anisotropy in the electronic distribution of a material. It may also indicate the bonding characteristics of the electrons. It is the calculation and interpretation of these Compton profile anisotropies that the MSC theory discussed in the next chapter focuses on.

C. Previous Calculations

As noted earlier there have been previous theoretical calculations of Compton profile anisotropies in some crystals. We describe below some of the more successful ones.

The tight-binding model was used by Berggren, Martino, Eisenberger, and Reed ^(7,9) to calculate the Compton profile anisotropies in LiF. Basic to this approach is the assumption that the Li^+ and F^- ions retain their ionic wavefunctions and participate in the crystalline environment only in the sense that there are overlaps in the wavefunctions between neighboring ions. If these overlaps are small (which is true for ionic solids) then the density matrix for the solid may be calculated as an expansion in terms of these overlaps. Enough terms are kept until convergence is assured.

Euwema, Wepfer, Surratt, and Wilhite ⁽⁸⁾ used a

crystal Hartree-Fock formalism with Gaussian-type orbitals (GTO) as local basis functions to calculate the anisotropies in crystalline neon and LiF. We compare our calculations on LiF with that of Berggren and Euwema in Chapter 3.

A self-consistent LCAO energy-band calculation was performed by Rath, Wang, Tawil, and Callaway ⁽¹¹⁾ on chromium, iron, and nickel to obtain the electronic momentum distribution and Compton profiles along the various crystalline directions. The basis consisted of a linear combination of GTO's in the form given by Wachters.

Snyder and co-workers ⁽¹²⁾ employed ab initio wavefunctions for small molecules to construct a simple model for the Compton profile of graphite and diamond. Pandey ^(12,13) used the pseudopotential or free-electron approach to study the same two materials. The most salient observation in these studies is that the localized molecular model predicts the anisotropy of the Compton profile of graphite about as well as the pseudopotential approach which is a crystalline calculation.

II. THEORY

Basic to the MSC procedure is the assumption that observed anisotropies have their origin in local rather than many-body interactions and can thus be associated almost entirely with the polar-covalent character of bonds between nearest-neighbor atoms. It is further assumed that the polarity and covalency of these bonds is primarily a function of the component atoms ⁽¹⁴⁾ and not particularly dependent on the phase, be it liquid, solid or vapor. As such, bonds in crystals should be well approximated by bonds in corresponding diatomic molecules provided appropriate symmetry modifications are made.

We proceed in the development of the MSC formalism by deriving equations for calculating Compton profiles in diatomic molecules along a momentum vector oriented at an arbitrary angle relative to the bond axis. We then describe a procedure of orienting the molecules in an array designed to simulate the momentum density observed in Compton scattering experiments when scattering along a particular crystal plane. Finally we modify the momentum density in a manner consistent with symmetry differences between the vapor and solid phases.

As a first step in our development we assume that the ground-state wavefunction for an N- electron system ⁽¹⁵⁾ is given by the single Slater determinant

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \frac{1}{\sqrt{N!}} \det \{ \phi_1, \phi_2, \dots, \phi_N \} \quad (\text{II-1})$$

where ϕ_i represents a molecular spin orbital (MO). A Fourier transformation of Ψ yields the corresponding groundstate momentum wavefunction

$$\chi(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) = \left(\frac{1}{2\pi}\right)^{\frac{3N}{2}} \int d^3x_1 \dots \int d^3x_N \cdot \exp[-i(\vec{p}_1 \cdot \vec{x}_1 + \dots + \vec{p}_N \cdot \vec{x}_N)] \Psi(\vec{x}_1, \dots, \vec{x}_N) \quad (\text{II-2})$$

We have set $\hbar=1$ in the equation above in conformity with the atomic units used in Compton profile work.

Using the orthonormality property of the MO'S,

$$\int d^3x \phi_i^*(\vec{x}) \phi_j(\vec{x}) = \delta_{ij} \quad (\text{II-3})$$

equation (II-2) may be cast in the form

$$\chi(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) = \frac{1}{\sqrt{N!}} \det \{ \chi_i, \chi_2, \dots, \chi_N \} \quad (\text{II-4})$$

where

$$\chi_i(\vec{p}) = \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \int d^3x e^{-i\vec{p} \cdot \vec{x}} \phi_i(\vec{x}) \quad (\text{II-5})$$

is the i^{th} momentum MO associated with the i^{th} position MO.

Since the χ_i 's are also orthonormal wavefunctions the total one-electron momentum density of the system obtained by squaring equation (II-4) and integrating over N-1 coordinates reduces to a sum over the probability densities of being in each allowed state. If we let ρ denote the total one-electron momentum density, then

$$\rho(\vec{p}) = \sum_{i=1}^N \rho_i(\vec{p}) \quad (\text{II-6})$$

where

$$\rho_i(\vec{p}) = \chi_i^*(\vec{p}) \chi_i(\vec{p}) \quad (\text{II-7})$$

is the momentum density due to the i^{th} MO.

If we define a particular direction in momentum space $\vec{p}'_z$ and integrate ρ over planes perpendicular to this direction, the resultant one-dimensional momentum distribution

$$J(p'_z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp'_x dp'_y \rho(\vec{p}) \quad (\text{II-8})$$

is what we have defined as the Compton profile in Chapter I, appropriate when the momentum-transfer vector is parallel to $\vec{p}'_z$. Differences in the profiles corresponding to different orientations of $\vec{p}'_z$ are what we have defined as Compton profile anisotropies.

A transformation is necessary to express the momentum density, $\rho(\vec{p})$ as a function of the primed coordinates. If α and β are the polar and azimuthal coordinates, respectively, of the $\vec{p}'_z$ axis with respect to the unprimed axes that define the momentum density ρ , the transformation has the form

$$p_x = \cos \alpha \cos \beta p'_x - \sin \beta p'_y + \sin \alpha \cos \beta p'_z \quad (\text{II-9a})$$

$$p_y = \cos \alpha \sin \beta p'_x + \cos \beta p'_y + \sin \alpha \sin \beta p'_z \quad (\text{II-9b})$$

$$p_z = -\sin \alpha p'_x + \cos \alpha p'_z \quad (\text{II-9c})$$

This transformation (see Figure 2) is most easily obtained by a rotation by the angle β about the ρ_z axis followed by a rotation by the angle α about the new ρ_r axis. The inverse transformation then yields equations (II-9a) to (II-9c) immediately. By using different values of α and β we are effectively changing the momentum-transfer direction relative to the bond-axis (in the case of a diatomic molecule) direction. The double integral indicated in equation (II-8) will then yield the Compton profile for any chosen direction. While this double integral cannot in general be done analytically it is a straightforward matter to do this numerically using Gauss-Legendre quadrature (we leave the details of this procedure to Appendix A).

For a diatomic molecule (AB) the i^{th} molecular orbital is assumed expressible as

$$\phi_i(\vec{X}) = \phi_i(\vec{X}_A) + \phi_i(\vec{X}_B) \quad (\text{II-10})$$

where $\phi_i(\vec{X}_A)$ are linear combinations of Slater type orbitals centered on nucleus A; a corresponding description applies to $\phi_i(\vec{X}_B)$.

The momentum-transform of this MO is given by

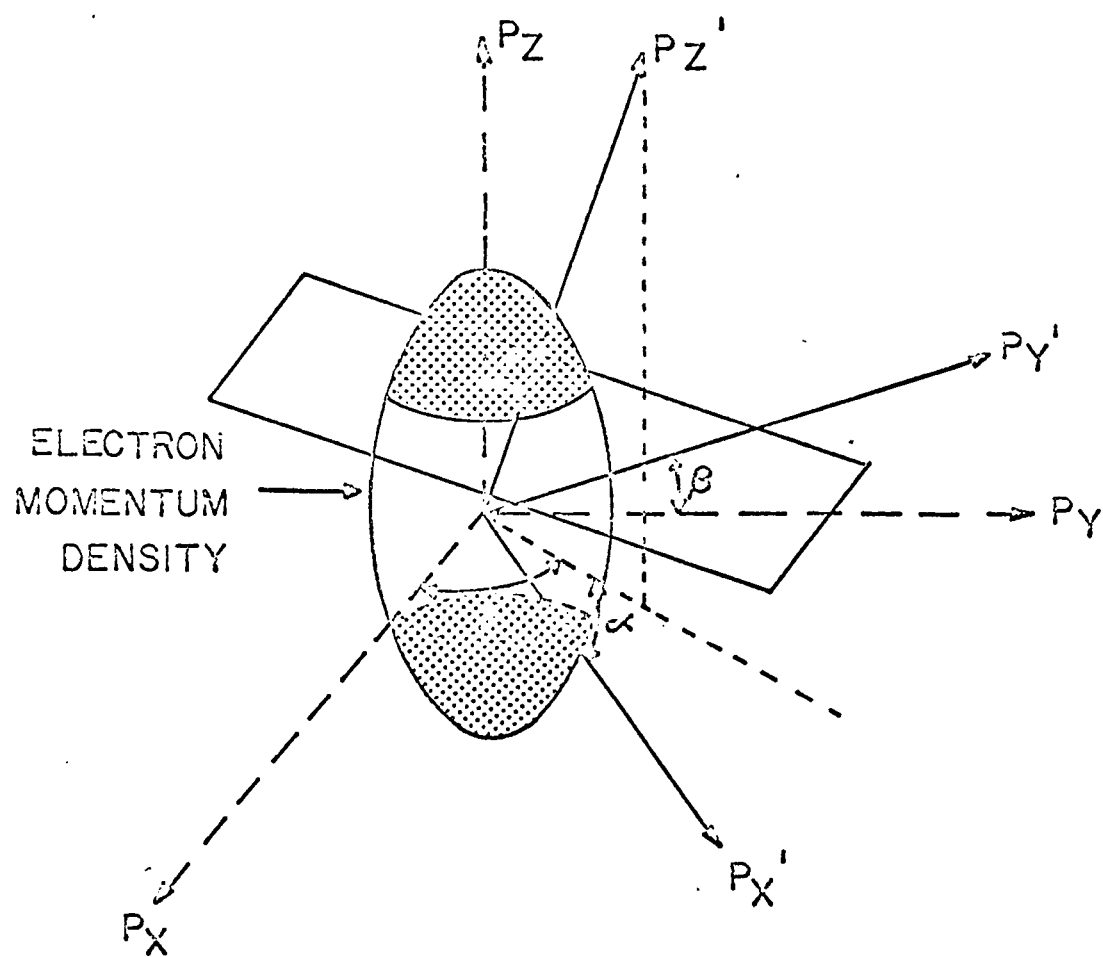
$$\chi_i(\vec{p}) = \left(\frac{1}{2\pi}\right)^{3/2} \int d\vec{X} e^{-i\vec{p}\cdot\vec{X}} [\phi_i(\vec{X}_A) + \phi_i(\vec{X}_B)] \quad (\text{II-11})$$

If we let the origin of $\vec{X}$ coincide with $\vec{X}_A$ the following result is obtained

$$\chi_i(\vec{p}) = \chi_i^A(\vec{p}) + e^{-i\vec{p}\cdot\vec{R}} \chi_i^B(\vec{p}) \quad (\text{II-12})$$

FIGURE 2

The primed and unprimed momentum coordinate systems. The angles α and β are also shown with the plane of integration normal to ρ'_z .



where

$$\chi_i^A(\vec{p}) = \left(\frac{1}{2\pi}\right)^{3/2} \int d^3\chi_A e^{-i\vec{p}\cdot\vec{\chi}_A} \phi_i(\vec{\chi}_A) \quad (\text{II-13})$$

and $\vec{R}$ is a radius vector from nucleus A to nucleus B whose magnitude is the inter-nuclear separation of the diatomic system.

To proceed further we require momentum transforms of the Slater orbitals,

$$\phi_{nlm}^{STO}(\vec{r}) = k_n e^{-\gamma r} r^{n-1} Y_l^m(\theta, \phi) \quad (\text{II-14})$$

where $k_n = (2\gamma)^{n+1/2} [(2n)!]^{-1/2}$ is the normalization factor and n, l , and m are the usual atomic quantum numbers. To get the Fourier transform we use the plane-wave expansion (16)

$$e^{-i\vec{p}\cdot\vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} (-i)^l j_l(pr) Y_l^m(\hat{p}) Y_l^{m*}(\hat{r}) \quad (\text{II-15})$$

where j_l is a spherical Bessel function of the first kind and Y_l^m is a spherical harmonic. The following result is obtained after using the orthonormality of the Y_l^m 's and integrating over the angles,

$$\chi_{nlm}^{STO}(\vec{p}) = (-i)^l \sqrt{\frac{2}{\pi}} k_n \left[\int_0^{\infty} dr r^{n+1} e^{-\gamma r} j_l(pr) \right] Y_l^m(\hat{p}) \quad (\text{II-16})$$

We note that for an STO the angular dependence is the same in both the position and momentum representations. The integral over r may be evaluated analytically for different n and l values with the use of the following recursion formulas,

$$\int_0^{\infty} dr r^{n+1} e^{-fr} j_0(pr) = \left(\frac{-d}{df} \right)^n \left(\frac{1}{f^2 + p^2} \right), n=1,2,\dots \quad (\text{II-17})$$

$$\int_0^{\infty} dr r^{n+1} e^{-fr} j_1(pr) = \left(\frac{-d}{df} \right)^{n-1} \frac{2p}{(f^2 + p^2)^2}, n=2,3,\dots \quad (\text{II-18})$$

$$j_{\ell+1}(pr) = (2\ell+1) \frac{j_{\ell}(pr)}{pr} - j_{\ell-1}(pr), \ell=1,2,\dots \quad (\text{II-19})$$

In Table I we show the results of these calculations for s, p, d, and f STO's. In Appendix B we show, as an example, the evaluation of equation (II-16) for a 3d STO.

For diatomic molecules the angular momentum component parallel to the bond-axis is a conserved quantity. This means that the constituent STO's for an MO (e.g., sigma or pi) will all have the same dependence on ϕ (m is a "good" quantum number). With this in mind and assuming that only s, p, d, and f STO's are used in the basis set, the momentum MO may be written as

$$\chi_i(\vec{p}) = \text{Re}[\chi_i(\vec{p})] + i \text{Im}[\chi_i(\vec{p})] \quad (\text{II-20})$$

where the real and imaginary parts are given by

$$\begin{aligned} \text{Re}[\chi_i(\vec{p})] = & \sum_{s,d} \chi_A^{\text{STO}}(\vec{p}) + \cos(\vec{p} \cdot \vec{R}) \sum_{s,d} \chi_B^{\text{STO}}(\vec{p}) + \\ & \sin(\vec{p} \cdot \vec{R}) \sum_{p,f} \chi_B^{\text{STO}}(\vec{p}) \end{aligned} \quad (\text{II-21})$$

and

$$\begin{aligned} \text{Im}[\chi_i(\vec{p})] = & \sum_{p,f} \chi_A^{\text{STO}}(\vec{p}) - \sin(\vec{p} \cdot \vec{R}) \sum_{s,d} \chi_B^{\text{STO}}(\vec{p}) + \\ & \cos(\vec{p} \cdot \vec{R}) \sum_{p,f} \chi_B^{\text{STO}}(\vec{p}) \end{aligned} \quad (\text{II-22})$$

TABLE 1

ELECTRON	POSITION STO	MOMENTUM STO
1s	$\phi = \sqrt{4\gamma^3} e^{-\gamma r} Y_{00}(\Omega)$	$\chi = \sqrt{\frac{8\gamma^3}{\pi}} \frac{2\gamma}{(\gamma^2+p^2)^2} Y_{00}(\Omega p)$
2s	$\phi = \sqrt{\frac{4\gamma^5}{3}} r e^{-\gamma r} Y_{00}(\Omega)$	$\chi = \sqrt{\frac{8\gamma^5}{3\pi}} \frac{6\gamma^2-2p^2}{(\gamma^2+p^2)^3} Y_{00}(\Omega p)$
3s	$\phi = \sqrt{\frac{8\gamma^7}{45}} r^2 e^{-\gamma r} Y_{00}(\Omega)$	$\chi = \sqrt{\frac{16\gamma^7}{45\pi}} \frac{24(\gamma^3-\gamma p^2)}{(\gamma^2+p^2)^4} Y_{00}(\Omega p)$
4s	$\phi = \sqrt{\frac{4\gamma^9}{315}} r^3 e^{-\gamma r} Y_{00}(\Omega)$	$\chi = \sqrt{\frac{8\gamma^9}{315\pi}} \frac{24(5\gamma^4-10\gamma^2 p^2+p^4)}{(\gamma^2+p^2)^5} Y_{00}(\Omega p)$
2p	$\phi = \sqrt{\frac{4\gamma^5}{3}} r e^{-\gamma r} \begin{bmatrix} Y_{10}(\Omega) \\ Y_{11}(\Omega) \end{bmatrix}$	$\chi = -i\sqrt{\frac{8\gamma^5}{3\pi}} \frac{8\gamma p}{(\gamma^2+p^2)^3} \begin{bmatrix} Y_{10}(\Omega p) \\ Y_{11}(\Omega p) \end{bmatrix}$
3p	$\phi = \sqrt{\frac{8\gamma^7}{45}} r^2 e^{-\gamma r} \begin{bmatrix} Y_{10}(\Omega) \\ Y_{11}(\Omega) \end{bmatrix}$	$\chi = -i\sqrt{\frac{16\gamma^7}{45\pi}} \frac{(40\gamma^2 p-8p^3)}{(\gamma^2+p^2)^4} \begin{bmatrix} Y_{10}(\Omega p) \\ Y_{11}(\Omega p) \end{bmatrix}$
4p	$\phi = \sqrt{\frac{4\gamma^9}{315}} r^3 e^{-\gamma r} \begin{bmatrix} Y_{10}(\Omega) \\ Y_{11}(\Omega) \end{bmatrix}$	$\chi = -i\sqrt{\frac{8\gamma^9}{315\pi}} \frac{(240\gamma^3 p-744\gamma p^3)}{(\gamma^2+p^2)^5} \begin{bmatrix} Y_{10}(\Omega p) \\ Y_{11}(\Omega p) \end{bmatrix}$
3d	$\phi = \sqrt{\frac{8\gamma^7}{45}} r^2 e^{-\gamma r} \begin{bmatrix} Y_{20}(\Omega) \\ Y_{21}(\Omega) \end{bmatrix}$	$\chi = -\sqrt{\frac{16\gamma^7}{45\pi}} \frac{48\gamma p^2}{(\gamma^2+p^2)^4} \begin{bmatrix} Y_{20}(\Omega p) \\ Y_{21}(\Omega p) \end{bmatrix}$
4f	$\phi = \sqrt{\frac{4\gamma^9}{315}} r^3 e^{-\gamma r} \begin{bmatrix} Y_{30}(\Omega) \\ Y_{31}(\Omega) \end{bmatrix}$	$\chi = i\sqrt{\frac{8\gamma^9}{315\pi}} \frac{348\gamma p^3}{(\gamma^2+p^2)^5} \begin{bmatrix} Y_{30}(\Omega p) \\ Y_{31}(\Omega p) \end{bmatrix}$

In both of these expressions the sums are over all the STO's with the given angular momentum.

The momentum density for the i^{th} MO is then

$$\rho_i(\vec{p}) = \text{Re}^2[\chi_i(\vec{p})] + \text{Im}^2[\chi_i(\vec{p})] \quad (\text{II-23})$$

From this expression and equations (II-21) and (II-22) we see that for certain momentum-transfer directions there will be enhancement in the momentum densities and therefore also in the directional Compton profiles. For the simplified case of one s-type STO centered on each atom the oscillations in the density are clearly seen to be due to the overlap between the STO's (see Appendix C). We also note that the momentum density ρ has cylindrical symmetry about the internuclear axis which we choose to be the p_z -axis. This means that the Compton profile will be independent of the angle β of the scattering vector. For a diatomic molecule the two most important momentum-transfer directions are the ones parallel and normal to the internuclear axis; these directions are equivalent to $\alpha=0^\circ$ and $\alpha=90^\circ$, respectively. The anisotropy of the Compton profiles in the molecule between these two directions, $J_0(\rho_z) - J_{90}(\rho_z)$ should be a good measure of the anisotropy in the electronic motion parallel and normal to the bond.

In the MSC procedure we choose $\vec{\rho}'_z$ vectors with angles appropriate to a particular crystal and plane. To simulate Compton profiles along 100, 110, and 111 planes in a face centered cubic lattice with a basis of two unlike atoms one at

(000) and one at ($\frac{1}{2}$ 00), we need four momentum transfer directions corresponding to $\alpha = 0^\circ$, 45° , 54.7° and 90° .

(See Figure 3) In terms of these angles we can write

$$\bar{J}_{100}(\rho'_z) = \frac{1}{3} J_0(\rho'_z) + \frac{2}{3} J_{90}(\rho'_z) \quad (\text{II-24a})$$

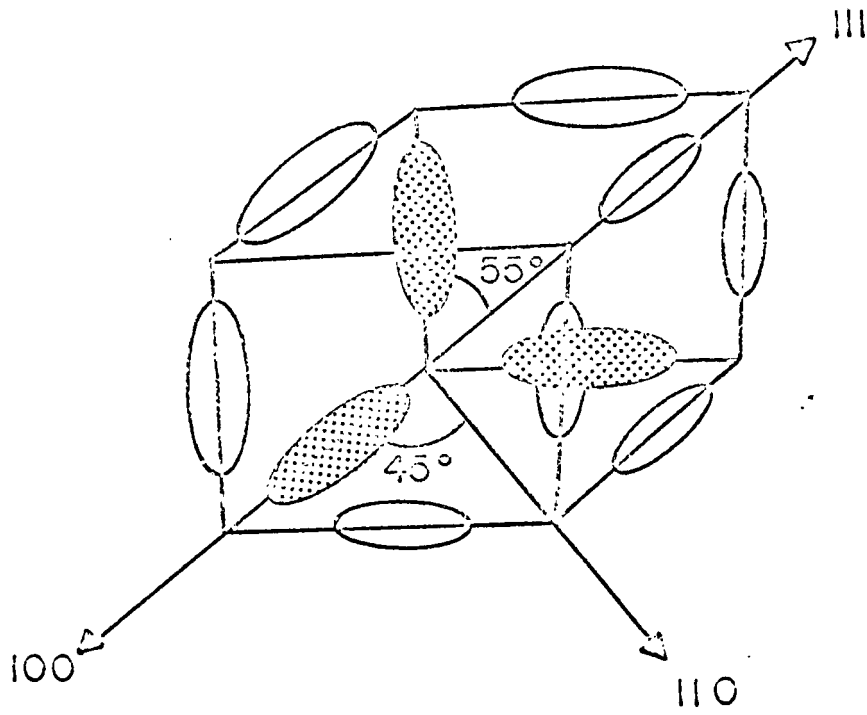
$$\bar{J}_{110}(\rho'_z) = \frac{1}{3} J_{90}(\rho'_z) + \frac{2}{3} J_{45}(\rho'_z) \quad (\text{II-24b})$$

$$\bar{J}_{111}(\rho'_z) = J_{54.7}(\rho'_z) \quad (\text{II-24c})$$

where $\bar{J}_{hkl}$ refers to a symmetry unresolved profile (SUP) along a particular plane. In this form the $\bar{J}$ represents the directional Compton profile for a crystal simulated by noninteracting diatomic molecules whose charge symmetry is appropriate to gas phase molecules. To write these equations we have taken cognizance of the fact that $\rho(\vec{p})$ is symmetric for $\pm \vec{p}$. Thus the polarity of the molecule (e.g., Li-F vs. F-Li) does not matter as far as the Compton profile is concerned. To obtain a realistic simulation of the crystal environment it is necessary to break down the π symmetry of the diatomic molecule and assume that the charge surrounding each atom is appropriate to the symmetry of the crystal lattice. This modification yields symmetry resolved profiles (SRP). Thus for example a symmetry resolved MSC profile J_{hkl} for LiF is that profile associated with the three non-interacting LiF molecules placed at right angles relative to each other, each having three equivalent $4\sigma^2$ orbitals emanating at right angles from the fluorine atom.

FIGURE 3

FCC geometry showing the three important crystallographic directions.



The anisotropy in the Compton profiles is given by

$$\Delta J(\rho'_z) = J_1(\rho'_z) - J_2(\rho'_z) \quad (\text{II-25})$$

which is just the difference between two Compton profiles associated with any two scattering directions. For an FCC crystal the three most important anisotropies are

$$\Delta J_1(\rho'_z) = J_{100}(\rho'_z) - J_{110}(\rho'_z) \quad (\text{II-26a})$$

$$\Delta J_2(\rho'_z) = J_{100}(\rho'_z) - J_{111}(\rho'_z) \quad (\text{II-26b})$$

and

$$\Delta J_3(\rho'_z) = J_{110}(\rho'_z) - J_{111}(\rho'_z) \quad (\text{II-26c})$$

In terms of the molecular Compton profiles these three anisotropies are given by

$$\Delta J_1 = \frac{1}{3} (J_0 - J_{90}) + \frac{2}{3} (J_{90} - J_{45}) \quad (\text{II-27a})$$

$$\Delta J_2 = \frac{1}{3} (J_0 - J_{54.7}) + \frac{2}{3} (J_{90} - J_{54.7}) \quad (\text{II-27b})$$

$$\Delta J_3 = \frac{1}{3} (J_{90} - J_{54.7}) + \frac{2}{3} (J_{45} - J_{54.7}) \quad (\text{II-27c})$$

We may also get an approximate spherically-averaged Compton profile from the MSC-SRP results for comparison to experimental results in polycrystalline samples. For FCC crystals this average is given by ⁽⁹⁾

$$\langle J \rangle = \frac{3 J_{100} + 6 J_{110} + 4 J_{111}}{13} \quad (\text{II-28})$$

III. APPLICATION TO LITHIUM FLUORIDE

A system that is particularly well suited for testing the procedures developed in the previous section and for obtaining an analysis of Compton profile anisotropies and their relationship to valence and core electrons is LiF. Near Hartree-Fock wavefunctions are available for this system (15) and experimental measurements and theoretical calculations of Compton profile anisotropies in the crystal have recently been reported. (7, 8, 9)

A. Molecular Compton Profile Anisotropies

To begin we investigate anisotropies parallel and perpendicular to the bond axis in the molecule performing calculations at an inter-nuclear separation of 3.55 a.u. (A wave function at the crystal separation of 3.798 a.u. was not readily available). The electronic configuration is $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$. All of the allowed molecular orbitals are fully occupied and on the basis of position density (18) and momentum density (19) calculations some total anisotropy should be evident.

In Figs. 4 and 5 we have plotted the Compton profiles for each occupied MO at the two angles $\alpha = 0^\circ$ and $\alpha = 90^\circ$ corresponding to momentum vectors parallel and normal to the bond, respectively. The plots are symmetric with respect to the vertical axis, i.e., $J(\rho'_z) = J(-\rho'_z)$. The Compton profiles per MO are normalized to

$$\int_{-\infty}^{\infty} d\rho'_z J(\rho'_z) = 1. \quad (\text{III-1})$$

FIGURE 4

Contribution of the occupied MO's of LiF to the Compton profile with the scattering axis parallel to the bonding direction. Each plot is normalized to one electron.

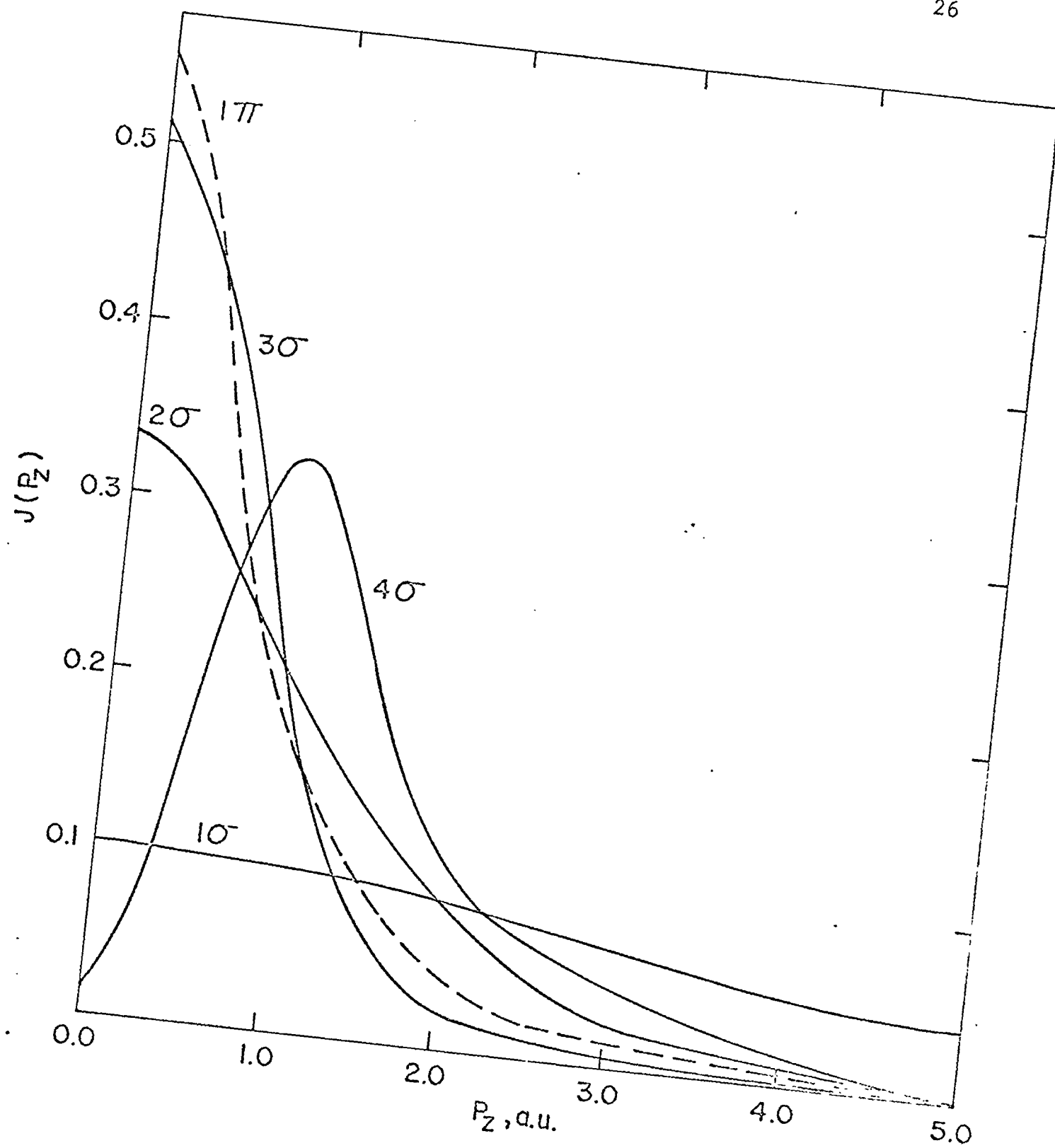
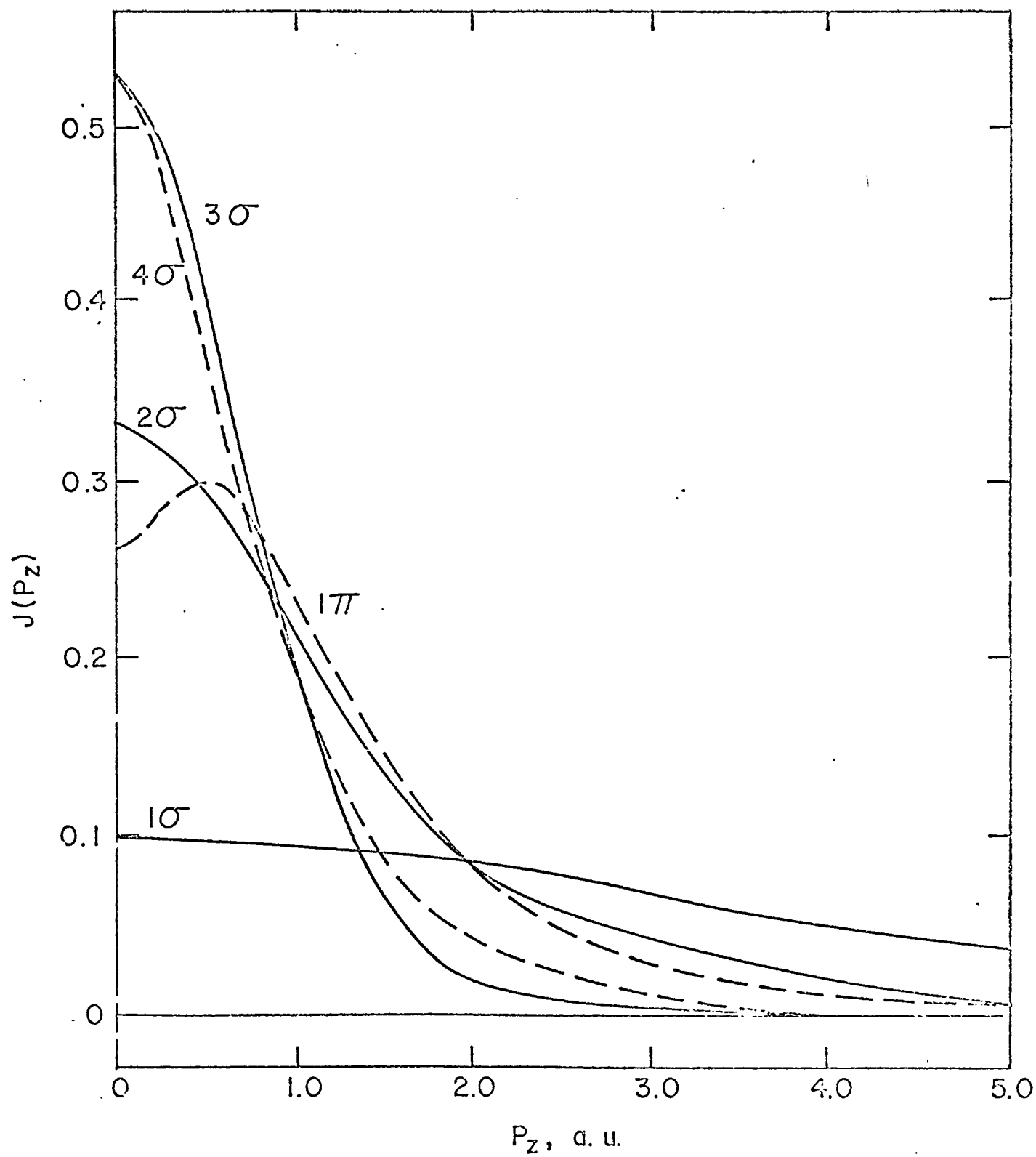


FIGURE 5

Contribution of the occupied MO's of LiF to the Compton profile with the scattering axis normal to the bonding direction. Each plot is normalized to one electron.



Thus, for any interval ρ'_z and $\rho'_z + \Delta\rho'_z$ the area under the curve is the probability of finding an electron whose momentum vector has its component along the vector defined by α in this range of ρ'_z .

Examination of the calculated Compton Profiles provides insight into electron momenta in a particular MO. The relative widths of profiles for various orbitals are indicative of the relative tightness of the binding of the MO. The 1σ , 2σ , and 3σ MO which correspond to the most tightly-bound electrons in LiF have very extended Compton profiles at both $\alpha = 0^\circ$ and $\alpha = 90^\circ$. This is not unexpected since the 1σ and the 3σ MO's are basically the $1s$ and $2s$ AO's of fluorine, respectively, and the 2σ MO is the $1s$ AO of lithium.

More interesting results are found in the 4σ and 1π MO which correspond to the $2p_\sigma$ and $2p_\pi$ orbitals of fluorine, respectively. The momentum density of that orbital has lobes similar to the lobes of the coordinate space electron density for the orbital. The lobes lie along the bond axis direction.

$J_0(\rho'_z = 0)$ is the integral of the momentum density over a plane normal to the bond axis and cutting the p_z -axis between the two lobes. Thus for the $2p_z$ orbital alone this quantity vanishes. The deviation from zero at $p_z = 0$ for the 4σ orbital with p'_z along p_z (seen in Fig. 4) is due to the s-type contributions to the MO, and is a measure of the charge shared in the bond. For $p'_z \neq 0$ the plane cuts through one of the lobes of $\rho(\vec{p})$ along the p_z -axis and the integrals, $J(p'_z)$,

increase to a maximum at $p'_z \approx 1$ a.u. and gradually drop off at higher values of p'_z . Comparison of the 4σ profiles in Figs. 4 and 5 points out the difference between integrating the momentum density over planes perpendicular to the bond axis as discussed above, and integrating over planes parallel to the bond axis which cut through both lobes of $\rho(\vec{p})$. As expected, the maximum value of $J(p'_z) \big|_{\lambda = 90^\circ}$ occurs for $p'_z = 0$, for which the plane of integration lies on the bond axis.

The 1π orbital has a great deal of $2p_x$ -like character, and the 1π Compton profiles in Figs. 4 and 5 exhibit that character. The p_x -like contributions have a directionally-dependent modulation factor for $\rho(\vec{p})$ which is a figure eight rotated about the p_z axis. Figure 4 gives $J(p'_z) \big|_{\lambda = 0^\circ}$. Here the planes of constant p'_z are normal to the p_z axis, and the result is that $J(p'_z) \big|_{\lambda = 0^\circ}$ for the 1π MO has its maximum at $p'_z = 0$. $J(p'_z) \big|_{\lambda = 90^\circ}$ involves planes which cut the rotated figure eight parallel to the p_z -axis, producing values of $J(p'_z) \big|_{\lambda = 90^\circ}$ which start with a nonzero value at $p'_z = 0$, increase to a maximum at about $p'_z = 0.5$ a.u., and then drop off more slowly than the values of $J(p'_z) \big|_{\lambda = 0^\circ}$ in Fig. 4. This behavior from the p_x -like contributions dominates the 1π profile in Fig. 5.

B. Crystalline Compton Profiles

Having discussed the shapes and genesis of anisotropies in the gas phase we can now proceed with a systematic analysis of anisotropies in crystals in terms of a molecular orbital

picture. Using Eqs. (II-24a) - (II-24c) we have computed symmetry unresolved profiles for LiF along the 100, 110 and 111 planes and plotted $4\bar{J}_1$ and $4\bar{J}_2$ anisotropies in Figs. 6 and 7, respectively. Contributions from each molecular orbital are shown. The dotted line corresponds to the experimentally observed anisotropy. These values are presented in Tables 2 and 3. These figures clearly illustrate the factors which contribute to the observed value. Consider Fig. 6. In the high momentum region the anisotropy associated with the 4σ orbital predominates. In this region the experimental curve has an intensity approximately three times that associated with the latter. This strongly suggests that each fluorine atom in the crystal is surrounded by six equivalent bonds having approximately 4σ molecular character. The peaks in the long range momentum region correspond almost totally to peaks in the sigma bonding orbital. At $p_z = 0$, the experimental anisotropy is slightly above zero. The $1\pi^4$ anisotropy is large and positive. This anisotropy largely vanishes in the crystal since the 1π electrons correlate with bonding sigma electrons. The anisotropy associated with the 3σ orbital reflects some polarization and hybridization of the $2s$ atomic orbital on fluorine. This 3σ anisotropy should be decreased in the crystal because the polarization decreases with inter-atomic spacing and because the symmetry of the crystal leads to less polarization.

In Fig. 7, where we have plotted $4\bar{J}_2$ anisotropies, a situation similar to that appearing in Fig. 6 is evident.

FIGURE 6

Contribution of the MO's of LiF to the 100-110 anisotropy. The dotted curve is the experimental result (Ref. 9). The 1σ MO has negligible anisotropy.

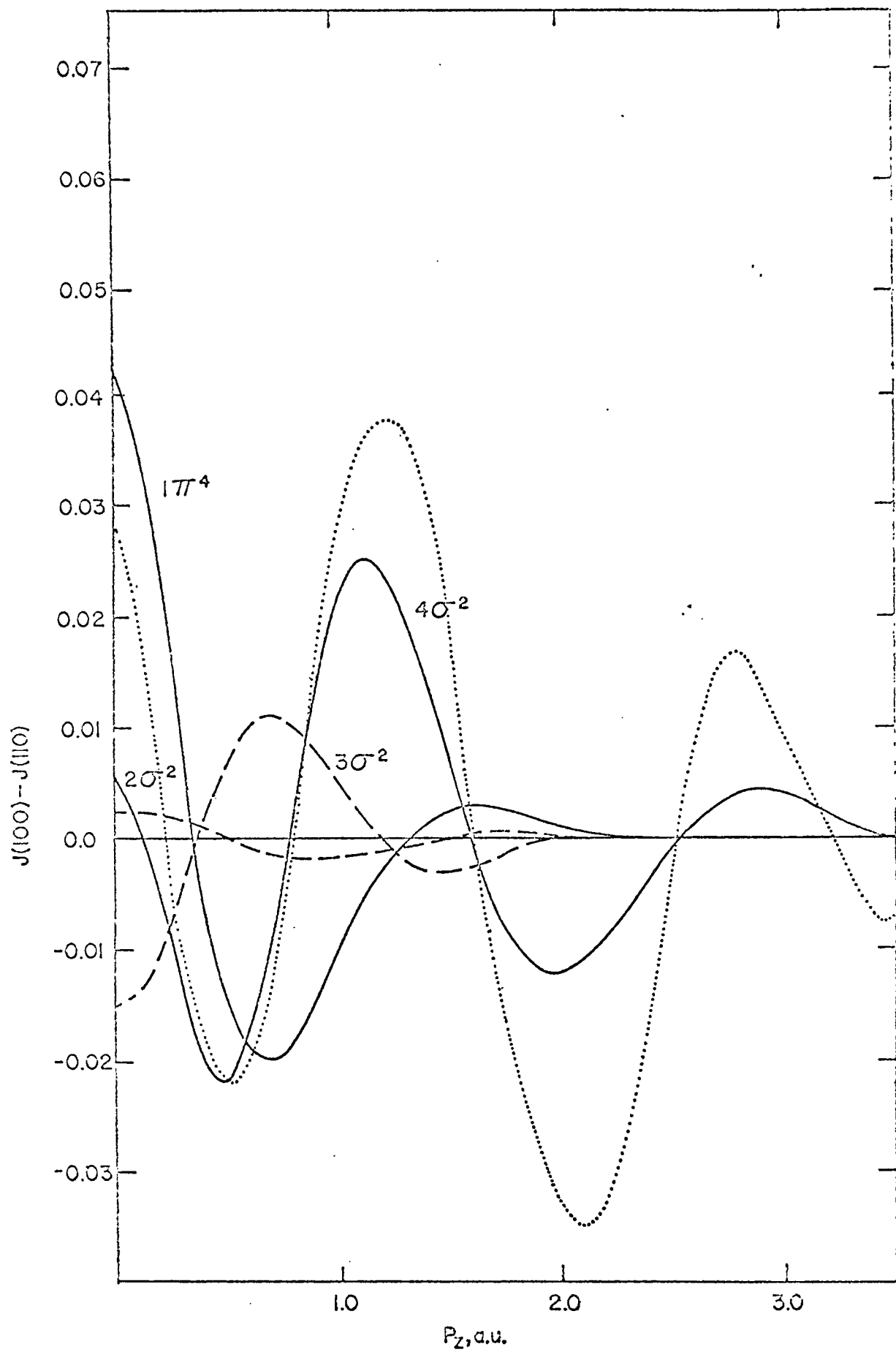


TABLE II
CONTRIBUTION OF EACH MO TO
THE $J_{100} - J_{110}$ ANISOTROPY IN LiF

$P_z, \text{a.u.}$	2σ	3σ	4σ	1π	EXP(a)
0.0	.0021	-.0151	.0049	.0409	.028
.1	.0021	-.0137	.0023	.0363	.018
.2	.0019	-.0098	-.0045	.0244	.003
.3	.0015	-.0043	-.0131	.0093	-.011
.4	.0010	.0015	-.0201	-.0041	-.019
.5	.0002	.0065	-.0224	-.0137	-.022
.6	-.0004	.0097	-.0187	-.0188	-.019
.7	-.0011	.0107	-.0094	-.0196	-.011
.8	-.0016	.0098	.0024	-.0180	.002
.9	-.0019	.0077	.0135	-.0147	.018
1.0	-.0018	.0047	.0216	-.0105	.030
.2	-.0014	-.0005	.0245	-.0031	.038
.4	-.0005	-.0031	.0139	.0012	.030
.6	.0001	-.0029	-.0001	.0031	.003
.8	.0004	-.0015	-.0096	.0027	-.021
2.0	.0005	-.0001	-.0119	.0017	-.033
.2	.0005	.0004	-.0087	.0009	-.033
.4	.0003	.0004	-.0033	.0003	-.015
.6	.0002	.0001	.0015	.000	.008
.8	-.0001	.0001	.0039	-.0003	.017
3.0	-.0001	.0001	.0039	-.0001	.010
.2	-.0002	.0002	.0023	.0000	.002
.4	-.0001	.0002	.0003	-.0001	-.006

(a) Total anisotropy (ref. 9)

FIGURE 7

Contribution of the MO's of LiF to the 100-111 anisotropy. The dotted curve is the experimental result (Ref. 9). The 1σ MO has negligible anisotropy.

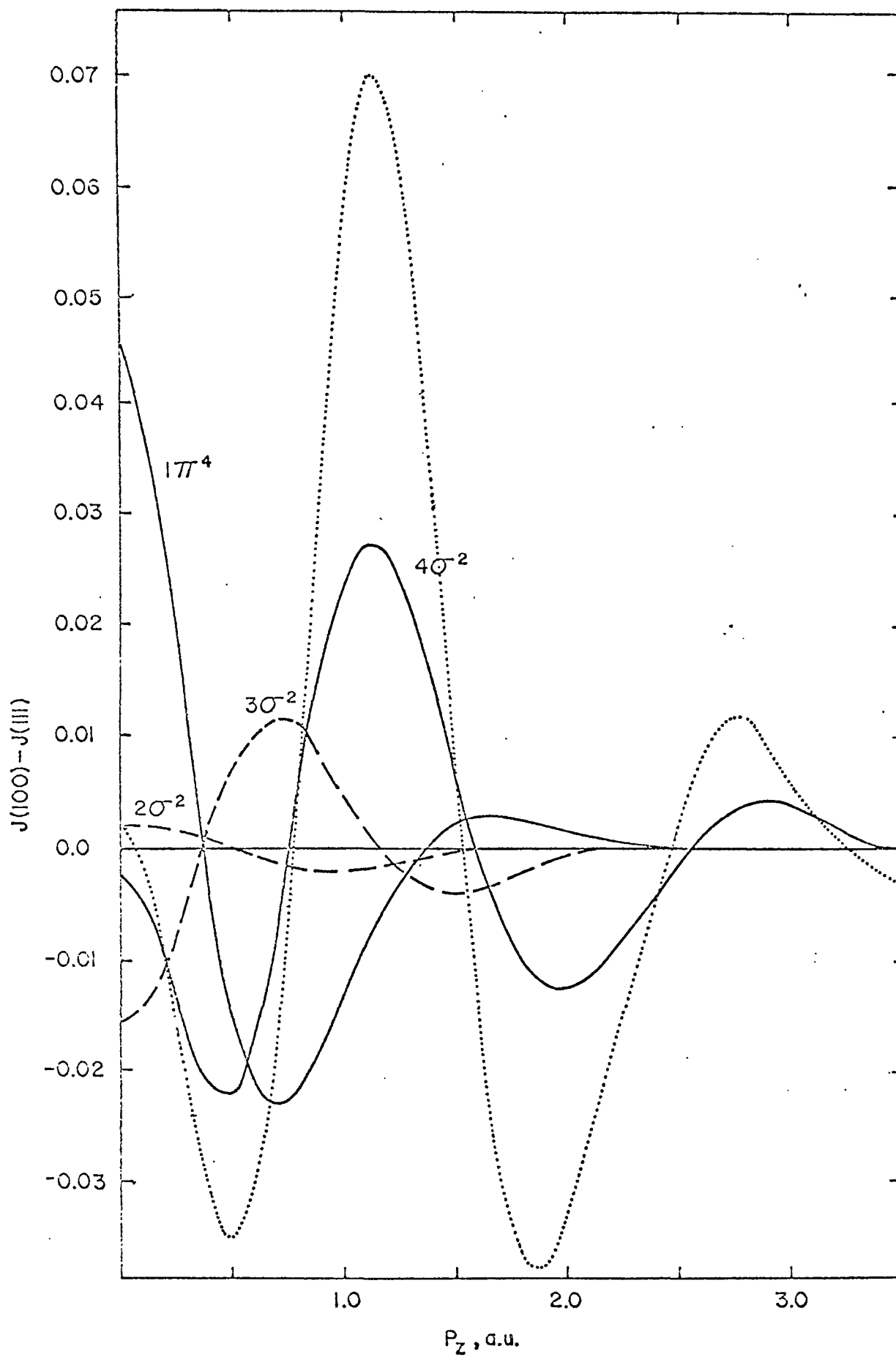


TABLE III
CONTRIBUTION OF EACH MO TO
THE $J_{100}-J_{111}$ ANISOTROPY IN LiF

P_z , a.u.	2 σ	3 σ	4 σ	1 π	EXP(a)
0.0	.0023	-.0155	-.0025	.0451	.002
.1	.0023	-.0141	-.0043	.0407	-.002
.2	.0020	-.0101	-.0098	.0285	-.012
.3	.0017	-.0043	-.0163	.0125	-.024
.4	.0011	.0019	-.0213	-.0029	-.032
.5	.0001	.0071	-.0223	-.0144	-.035
.6	-.0005	.0103	-.0173	-.0208	-.029
.7	-.0012	.0115	-.0075	-.0228	-.015
.8	-.0017	.0105	.0049	-.0208	.008
.9	-.0021	.0083	.0163	-.0175	.036
1.0	-.0020	.0051	.0241	-.0127	.059
.2	-.0015	-.0007	.0265	-.0039	.067
.4	-.0005	-.0035	.0148	.0011	.031
.6	.0001	-.0031	.0000	.0031	-.015
.8	.0005	-.0018	-.0099	.0027	-.037
2.0	.0006	-.0001	-.0125	.0023	-.033
.2	.0005	.0004	-.0092	.0011	-.018
.4	.0004	.0005	-.0037	.0001	-.005
.6	.0001	.0004	.0013	-.0001	.008
.8	-.0001	.0005	.0037	-.0003	.012
3.0	-.0002	.0003	.0036	.0001	.006
.2	-.0003	.0005	.0021	.0001	.002
.4	-.0001	.0004	.0001	.0000	-.002

(a) Total anisotropy (ref. 9)

The long range component of the anisotropy can clearly be associated with electrons in 4σ orbitals. The experimental anisotropy at $p_z = 0$ is fairly large and positive. This result reflects a corresponding 4σ anisotropy. The magnitude of the experimental anisotropy in the high momentum region corresponds closely to that expected for a fluorine ion possessing six singly occupied 4σ bonds at right angles to each other with charge distributions similar to that found in the gas phase. As a reflection of this fact we thus construct total profiles by ignoring the valence shell 1π contributions and multiplying $4\sigma^2$ contributions by a factor of three. The resultant profiles we refer to as symmetry resolved profiles (SRP).

C. Comparison with Experiment.

We are now in a position to compare our calculated anisotropies with experimental curves and with other theoretical curves. This is done in Figs. 8 and 9 where we plot ΔJ_1 and ΔJ_2 . Included in the figures are MSC-SRP anisotropies at approximately the crystal spacing with the $3\sigma^2$ polarization contributions neglected for the crystalline environment, the experimental curve, and the theoretical curves of Berggren, Martino, Eisenberger and Reed (9) obtained in the tight binding approximation and of Euwema, Wepfer, Surratt, and Wilhite (8) based on a crystalline SCF calculation using a Gaussian basis set. Our curves compare favorably with both the experimental curve and the two theoretical curves. The MSC-SRP results are presented in Table 4. The

FIGURE 8

Experimental result and resolution-broadened theoretical 100-110 anisotropies in LiF. The solid curve is the experimental result (Ref. 9). The dotted curve is from Euwema (Ref. 8). The short dashed curve is from Berggren (Ref. 9). The long-dashed curve is the MSC-SRP result.

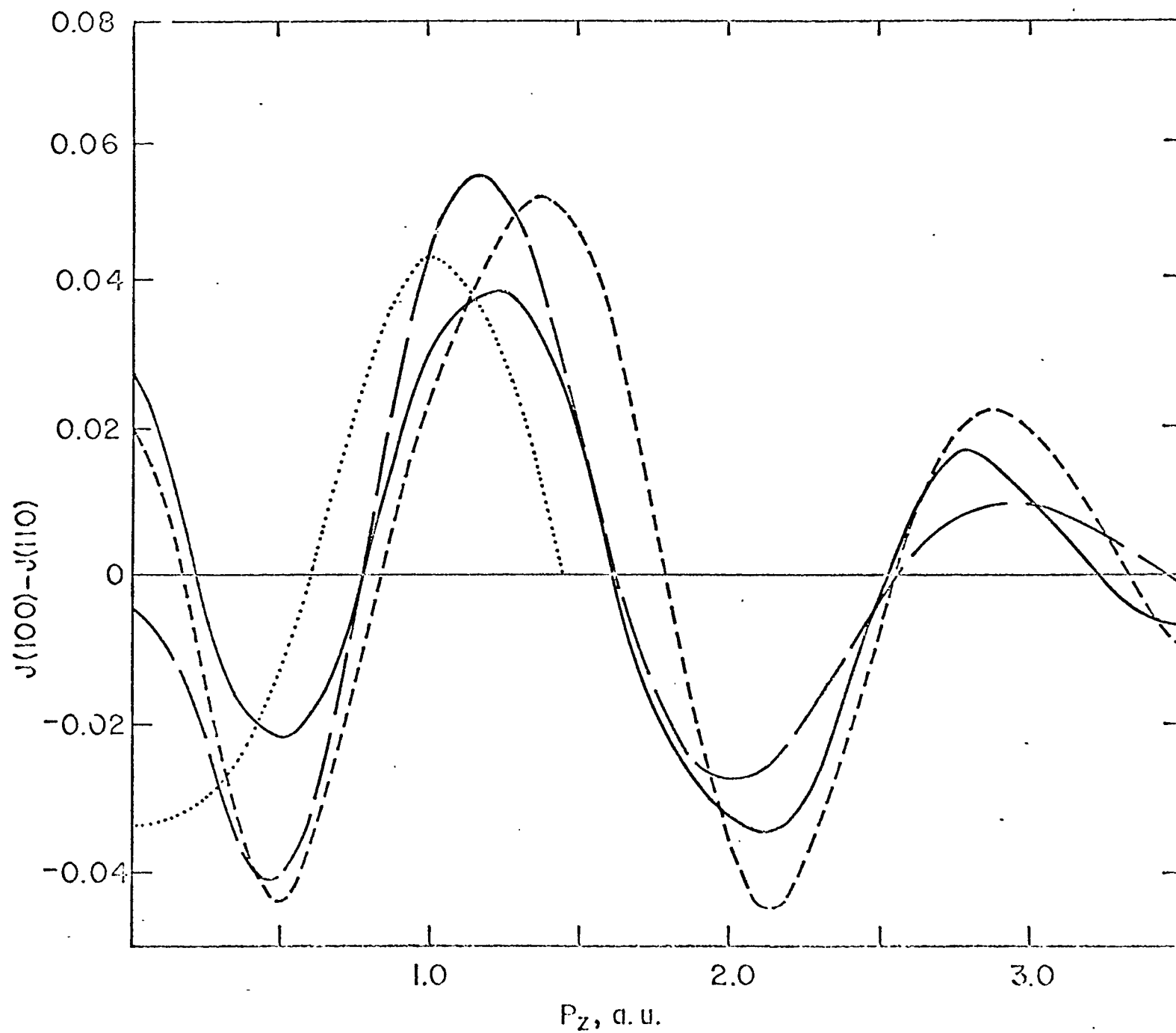


FIGURE 9

Experimental result and resolution-broadened theoretical 100-111 anisotropies in LiF. The solid curve is the experimental result (Ref. 9). The dotted curve is from Euwema (Ref. 8). The short-dashed curve is from Berggren (Ref. 9). The long-dashed curve is the MSC-SRP result.

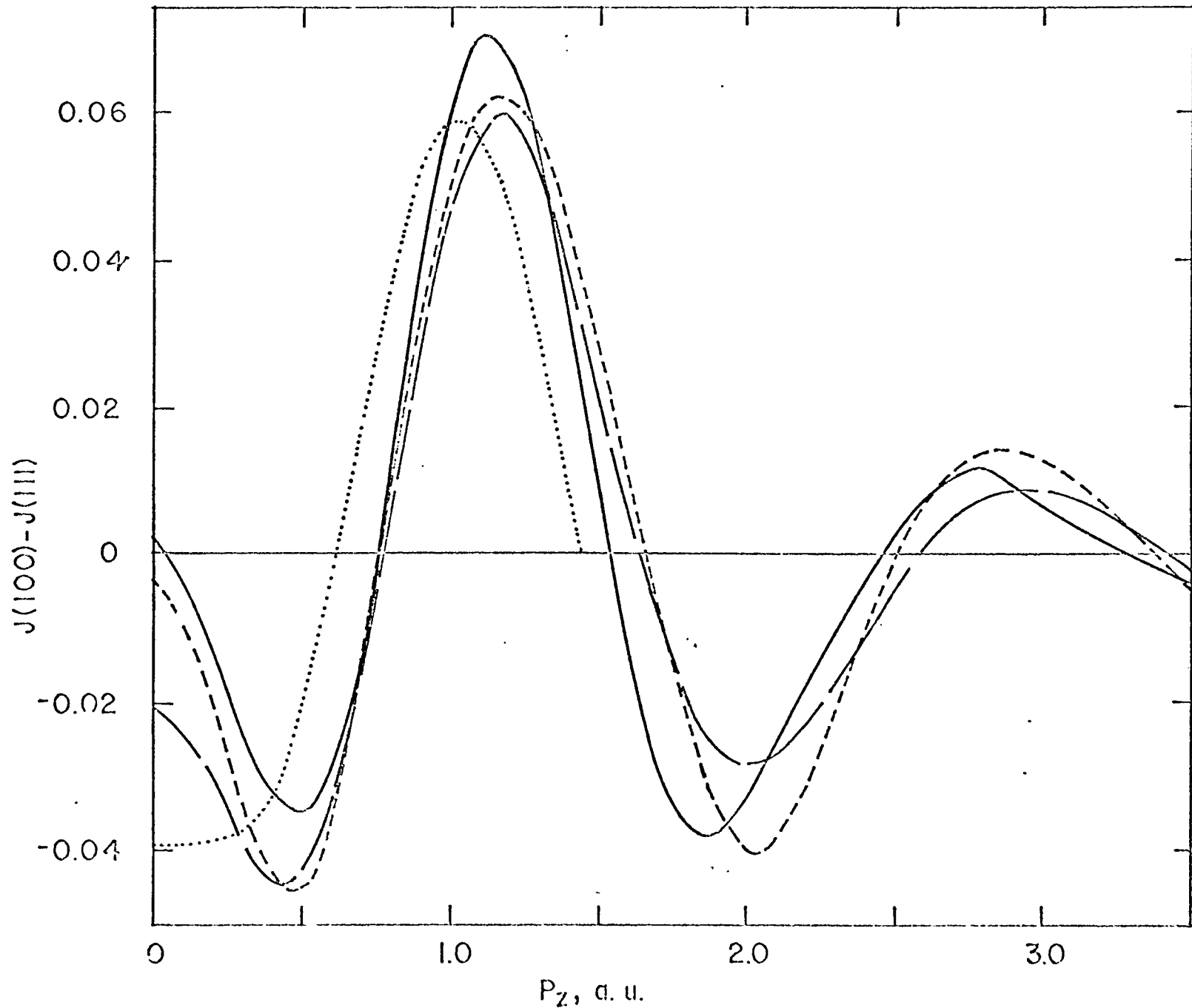


TABLE IV

MSC-SRP Theoretical Results for ΔJ_1 and ΔJ_2
in LiF at Internuclear Separation of 3.55 a.u.

P_z	$J_{100}-J_{110}$	$J_{100}-J_{110}$ Convolved with Resolution Function	$J_{100}-J_{111}$	$J_{100}-J_{111}$ Convolved with Resolution Function
0.0	+0.0166	-0.0046	-0.0052	-0.0207
0.1	+0.0091	-0.0083	-0.0107	-0.0235
0.2	-0.0117	-0.0180	-0.0274	-0.0307
0.3	-0.0380	-0.0298	-0.0472	-0.0390
0.4	-0.0592	-0.0387	-0.0630	-0.0440
0.5	-0.0670	-0.0403	-0.0667	-0.0432
0.6	-0.0564	-0.0327	-0.0524	-0.0339
0.7	-0.0292	-0.0166	-0.0236	-0.0169
0.8	+0.0056	+0.0045	-0.0129	+0.0050
0.9	+0.0385	+0.0257	+0.0466	+0.0275
1.0	+0.0630	+0.0427	+0.0702	+0.0459
1.1	+0.0740	+0.0522	+0.0808	+0.0564
1.2	+0.0720	+0.0534	+0.0779	+0.0530
1.3	+0.0596	+0.0469	+0.0636	+0.0506
1.4	+0.0410	+0.0348	+0.0438	+0.0375
1.5	+0.0197	+0.0199	+0.0209	+0.0215
1.6	-0.0003	+0.0047	+0.0001	+0.0053
1.7	-0.0167	-0.0087	-0.0175	-0.0088
1.8	-0.0284	-0.0188	-0.0293	-0.0195
1.9	-0.0342	-0.0250	-0.0355	-0.0261
2.0	-0.0354	-0.0271	-0.0371	-0.0284
2.2	-0.0253	-0.0216	-0.0267	-0.0231
2.4	-0.0091	-0.0095	-0.0101	-0.0109
2.6	+0.0049	+0.0020	+0.0043	+0.0008
2.8	+0.0119	+0.0085	0.0113	+0.0076
3.0	+0.0115	+0.0094	0.0109	+0.0087
3.2	+0.0068	+0.0062	0.0064	+0.0057
3.4	+0.0011	+0.0016	0.0007	+0.0012

major shortcoming in our results vis-a-vis the experimental results is our apparent over estimation of the peak intensity at $p_z = 1.2$ and 0.5 in the (100-110) anisotropy. We are not certain about the source of this discrepancy.

We also do not fare particularly well in predicting the non-bonding 110-111 anisotropy. In contrast, the other methods are normally most successful in predicting non-bonding anisotropies. The reason for this is probably due to the fact that our approach concentrates on the anisotropy associated with nearest neighbor bonds. Slight distortions due to second nearest neighbor interactions are expected. It is these distortions which contribute primarily to the 110-111 anisotropies. A crystal perturbation calculation with symmetric ions as the zeroth order state is capable of describing second nearest neighbor interactions as a first order perturbation correction. However, the description is general and difficult to associate with particular bonds.

IV. APPLICATION TO LITHIUM HYDRIDE

We shall apply the MSC formalism next to the lithium hydride molecule and crystal. LiH is a more covalent molecule than LiF, so this study should provide a good basis for the comparison of Compton profile anisotropies in diatomic crystals vis-a-vis the ionicity of the corresponding molecules. Also, experimental results for LiH Compton profile anisotropies are available for comparison to our theory. Unfortunately no other theoretical calculations of the anisotropies in LiH

crystal are available for comparison. One reason for this is maybe the fact that since LiH is more covalent than LiF the tight-binding approximation may not be as accurate since the overlap term in the density matrix for LiH is much larger than in LiF and thus has to be carried to higher order before it converges.

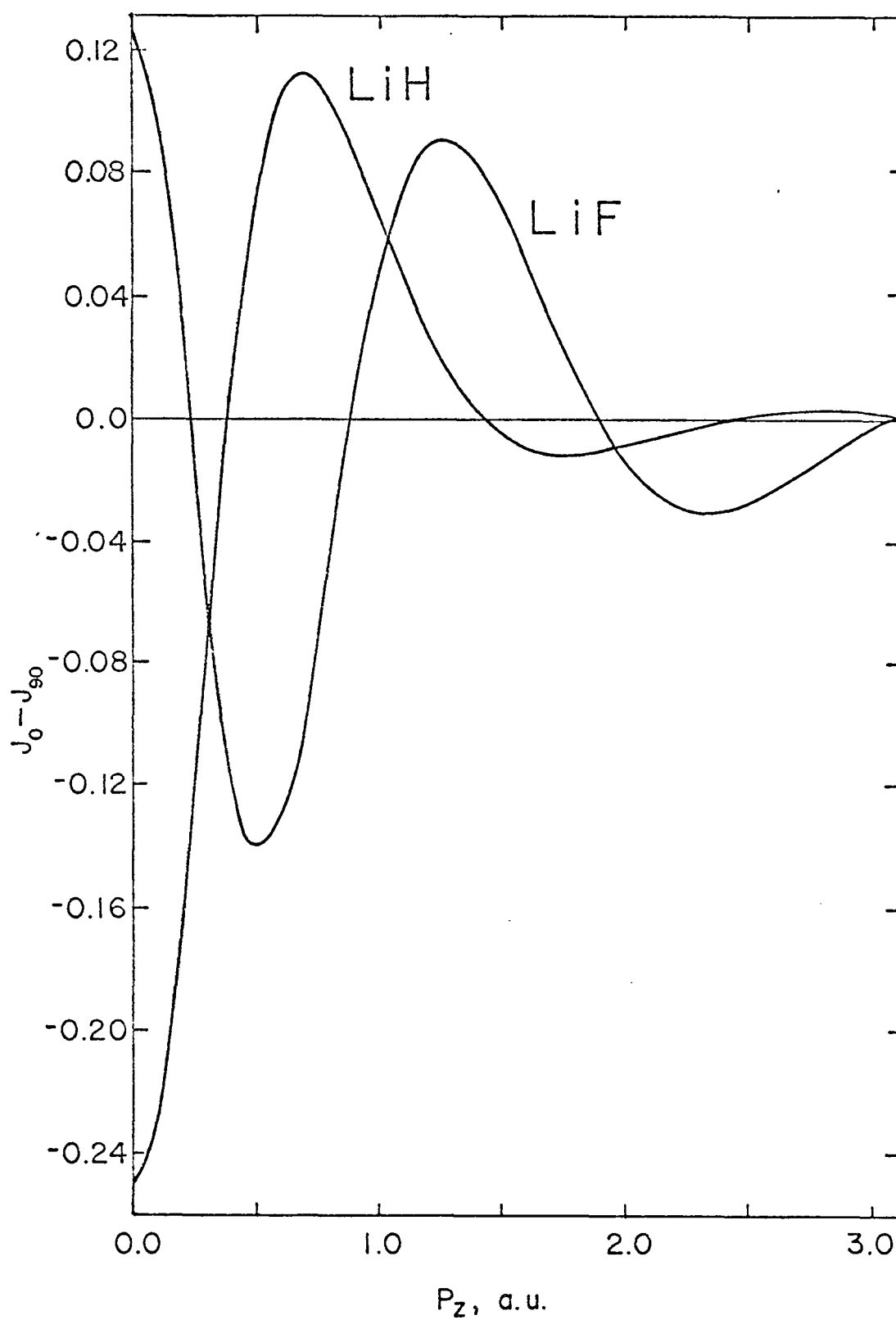
A. Molecular Anisotropies.

Molecular bonding nature is most clearly seen in the comparison of profiles calculated for p_z parallel, and perpendicular to the bond axis, $J_0(p_z)$ and $J_{90}(p_z)$ respectively. In Fig. 10 we present the difference profile $\Delta J(p_z) = J_0(p_z) - J_{90}(p_z)$ for the LiH molecule calculated using the SCF-LCAO-MO wavefunction of Cade and Huo (20) at $R_e = 3.015$ a.u.. We also present the corresponding anisotropy for the LiF molecule at the equilibrium spacing, $R_e = 2.9877$ a.u.. Differences between the LiF and the LiH figures are closely related to differences between the polarities and covalent characters of these bonds. For example, the more polar the bond, the less spreadout is the charge distribution. This leads to a low uncertainty in the bonding electrons' locations and a high uncertainty as to their energies and momenta. It appears that the further spreadout the major peaks in the ΔJ figure, the more polar and less covalent the bond.

Of particular interest is $\Delta J(0)$, the difference profile at $p_z = 0$. For LiF is positive, while for LiH it is

FIGURE 10

The 0 - 90 anisotropy in LiH and LiF. The curves correspond to LiF at the molecular equilibrium spacing of 2.9877 a.u. and LiH at 3.015 a.u.



negative and of larger magnitude. To understand this it is necessary to examine the changes occurring in the bonding molecular orbital when a positive and a negative ion combine to form a polar molecule.

Consider first LiF. Bonding in this molecule can be viewed as resulting from a partial transfer of a p_z electron on F^- to an orbital on Li^+ having both s and p_z character. Since s electrons have equal probabilities of moving $\perp$ and $\parallel$ to the bond while p_z electrons have considerably greater probability of moving $\parallel$ to the bond, the result of charge transfer is to decrease $\parallel$ motion and increase $\perp$ motion. Since $J_0(0)$ and $J_{90}(0)$ are respectively measures of the $\perp$ and $\parallel$ motions, $J_0(0) - J_{90}(0)$ is positive in LiF.

Now consider LiH. This bond can be viewed as forming from the partial transfer of an s electron on H^- to an orbital on Li^+ having both s and p_z character. The result of this transfer is to decrease the $\perp$ motion and increase the $\parallel$ motion of the bonding electron. Consequently $J_0(0) - J_{90}(0)$ is negative. We thus have the seemingly paradoxical situation that the more covalent the bond in alkali hydrides the more negative should be $J_0 - J_{90}$, while the more covalent the bond in alkali halides the more positive should be $J_0(0) - J_{90}(0)$. The relative positions of the intercepts should be an excellent measure of the relative polarity of the bonds.

B. Molecular Simulated LiH Crystal

Using our MSC procedure, we have calculated Compton

profiles for the principal crystallographic directions in LiH. In an LiH crystal, enhancement of the π bonds by replacement of crystal-symmetry violating π bonds does not occur, as it does in LiF.

Calculations of MSC Compton profile anisotropies for a LiH crystal were made using two sets of molecular orbitals at the molecular equilibrium spacing. The MO's of Cade and Huo (20) have a larger set of basis Slater type orbitals than that of R. Sahni et al. (21). Cade and Huo have taken better account of polarization by their inclusion of d and f STO's in their calculation. However, the two sets of MO's yield orbital energies which agree to three decimal figures. As seen in Figs. 11 and 12, the two sets of molecular orbitals give very similar results for the 100-110 and 100-111 anisotropies.

Experimental data points from Phillips and Weiss (22) are indicated in Fig. 11. This early experiment stressed the total profile rather than anisotropies, and its counting statistics were not sufficient to measure the anisotropies accurately. An experimental anisotropy is the difference between two measurements, thus having the errors of both, and the maximum anisotropy calculated for the crystal is approximately 2% of the maximum profile height, so extremely accurate measurements are necessary. The data points shown are differences between two points, each with an estimated error of $\pm .02$. General agreement between our theoretical

FIGURE 11

The 100 - 110 anisotropy in LiH. The full curve is the MSC result using Cade-Huo's MO's (Ref. 20); the dashed curve is MSC using Sahni's MO's (Ref. 21); the x's are the experimental results from Phillips (Ref. 22).

100-110 LiH

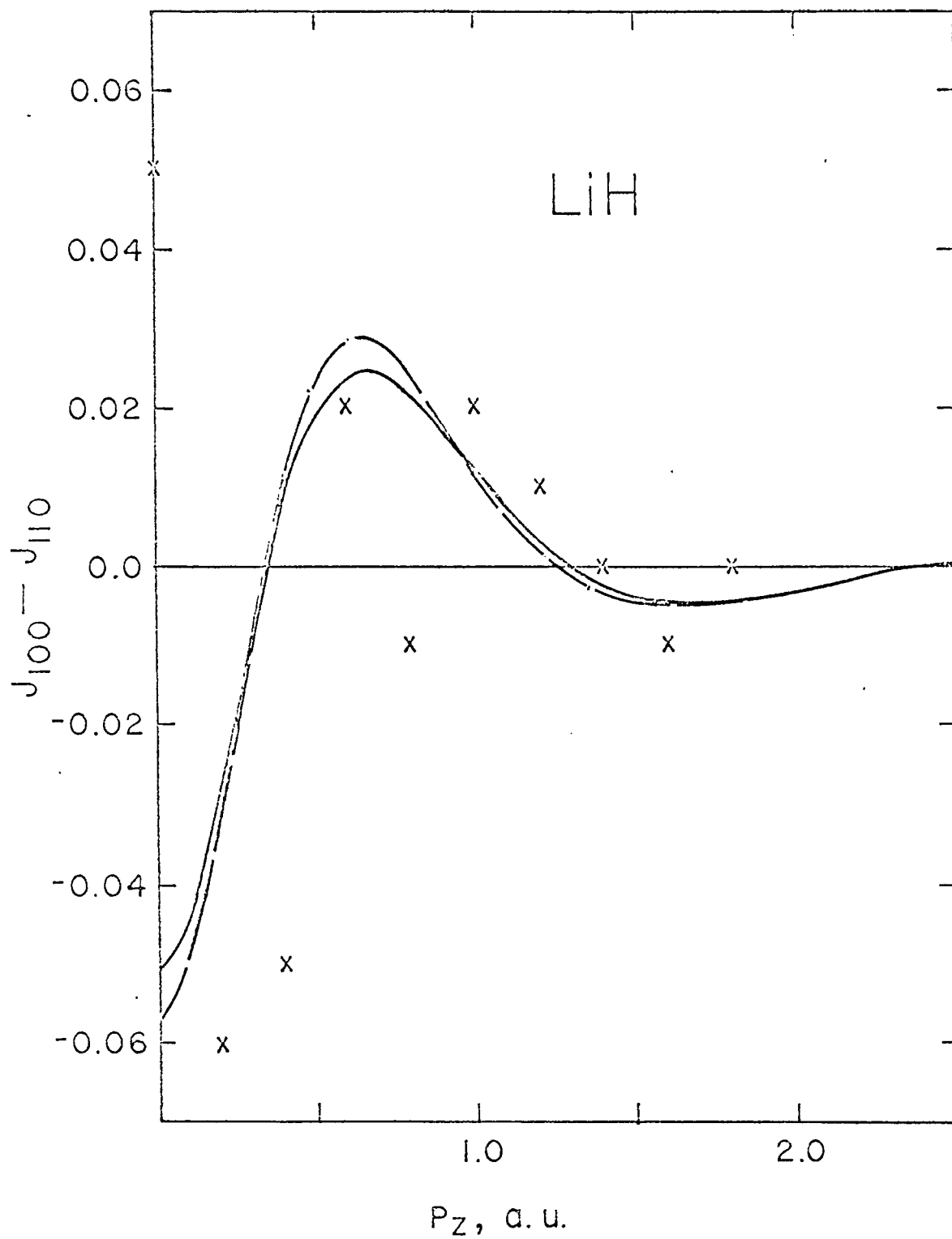
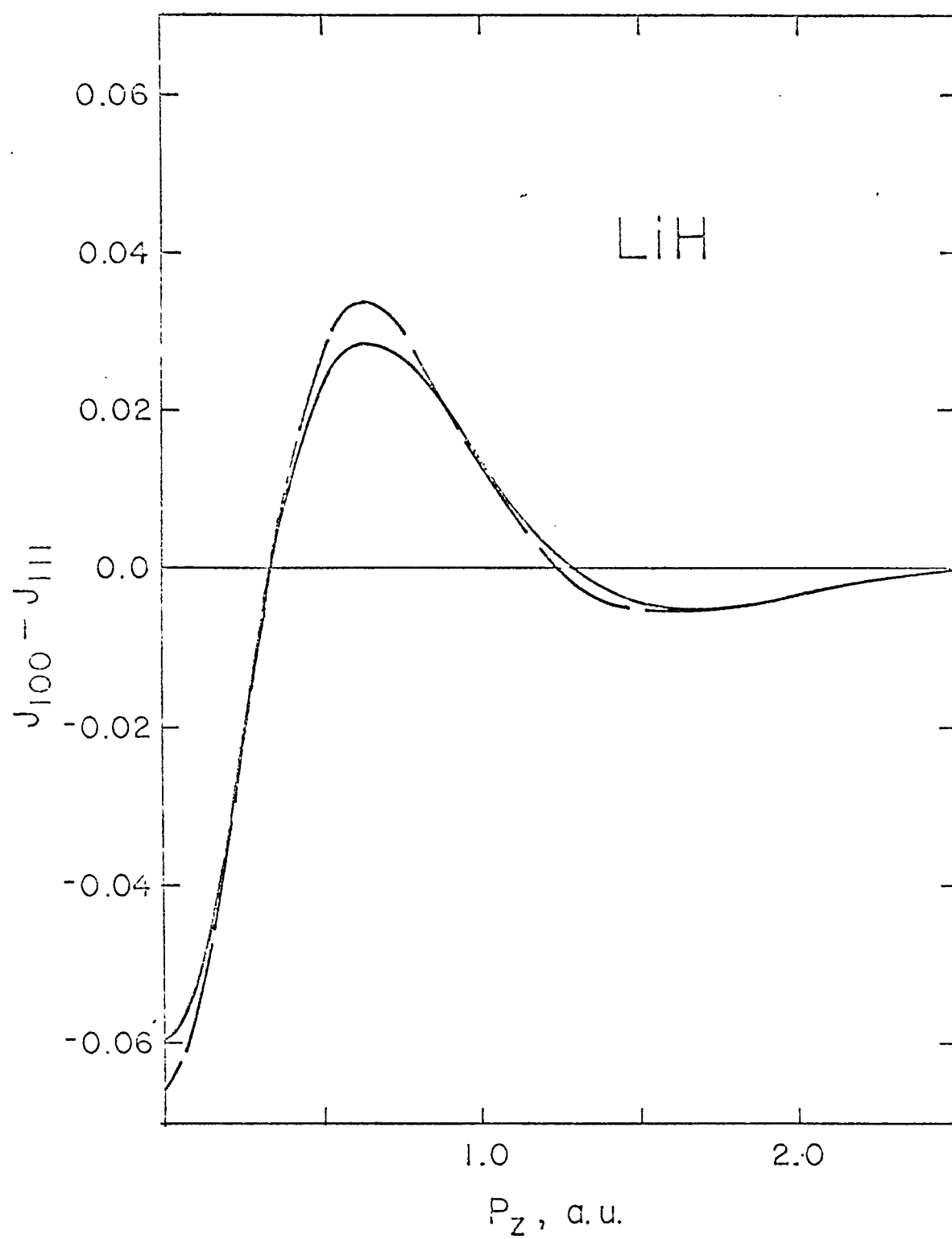


FIGURE 12

MSC results for the 100 - 111 anisotropy in LiH. The full curve is obtained using Cade-Huo's MO's (Ref. 20); the dashed curve is obtained when Sahni's MO's are used (Ref. 21); no experimental data are available.

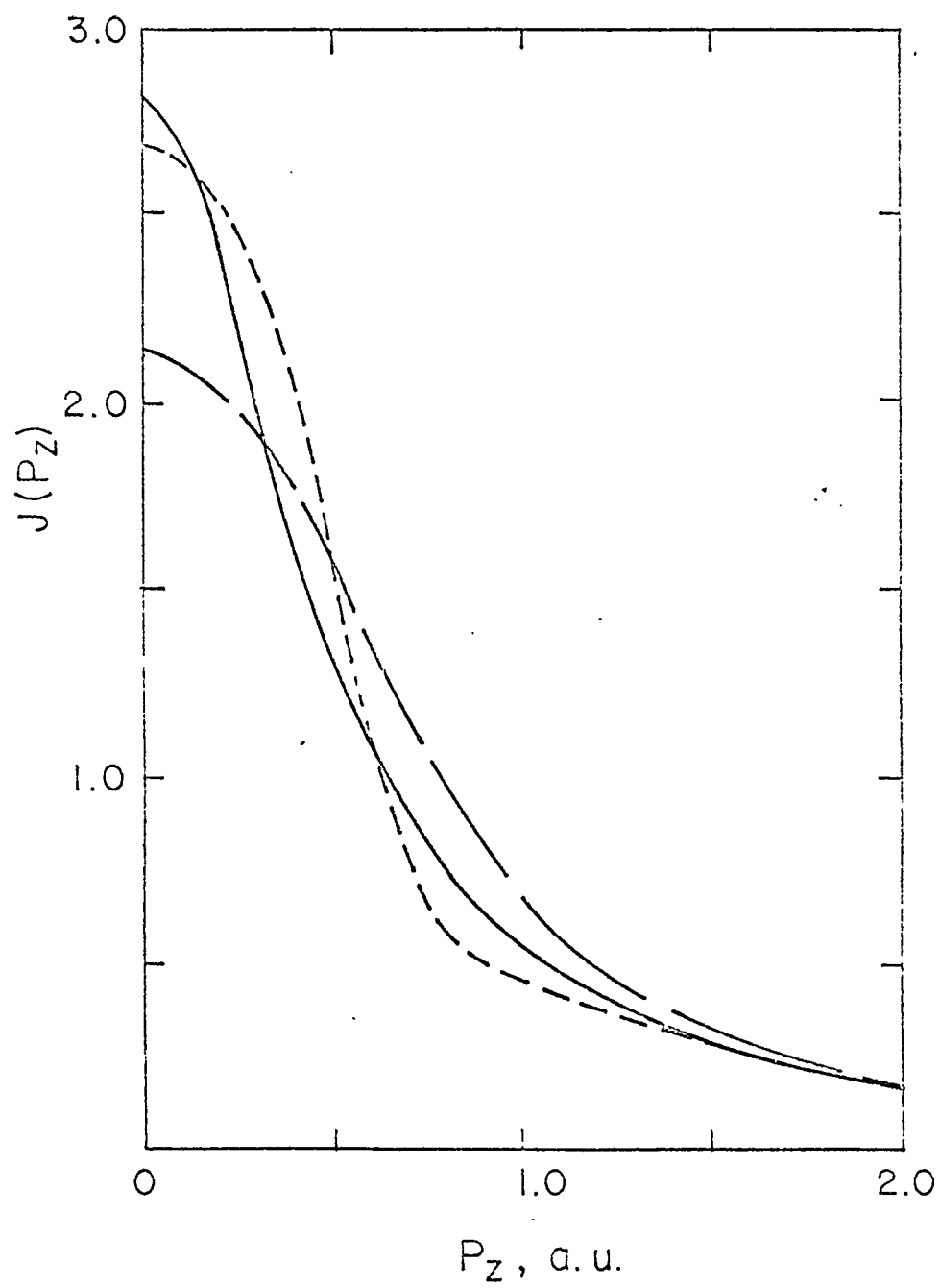


calculations and the data is seen with the exception of the point at $p_z = 0$. From the discussion above it is clear that this point is crucial to the interpretation of our theoretical results. Our calculations suggest that this experimental point is in error, and that a more accurate measurement over the entire range of interest is needed for comparison to theory. There is no experimental data for comparison to our results in Fig. 12.

Our averaged Compton profile, the averaged experimental results, (22) and theoretical results of Brandt (23) are presented in Fig. 13. The theoretical results, based on molecular orbital wavefunctions for a LiH molecule, are in better agreement with the data than are results of theories based on free Li and H neutral atoms, and free Li^+ and H^- ions. (24) Our fit is not as good as that of Berggren and Martino (25) who used a tight-binding wavefunction and included overlap between hydrogen atoms. The theoretical results of Brandt, (23) who used self-consistent electron wavefunctions for the LiH crystal in the cell approximation, are in better agreement with our results than either the experimental data or the results of Berggren and Martino (25). In light of recent discoveries of the importance of secondary scattering effects in work on samples with low photoelectric absorption coefficients, (26,27,28) the experimental LiH profile may be too wide and therefore too low at $p_z = 0$. Our results and those of Brandt (23) indicate that the profile may be higher at $p_z = 0$. A measurement of the profile of

FIGURE 13

Spherically averaged Compton profile for LiH: short-dashed curve is from a calculation by Brandt (Ref. 7), full curve is the MSC result using MO's from Ref. 20, and the long-dashed curve is the experimental data (Ref. 7).



polycrystalline LiH using Am-241 gamma rays also has $J(0)$ quite low, (29) probably because of multiple scattering effects.

Our theoretical calculations with two different sets of molecular orbitals for LiH molecules indicate that the 100-110 Compton profile anisotropy in LiH is large and negative at $p_z = 0$. These results suggest that another experimental measurement of Compton profiles in LiH should be made with emphasis on the anisotropies, using one of the new techniques for removal of multiple scattering effects in the data.

It is interesting to note a fundamental difference between the MSC representations of LiH and LiF crystals. In LiF the MSC procedure changes the 1σ electronic orbitals to oriented 4σ -like orbitals, and this modifies the crystalline anisotropies, enhancing the anisotropies, particularly for $p_z > 1.0$ a.u. For LiH no such enhancement should occur; there are no loosely bound electrons available to build enhancing bonding orbitals in the crystal. Although the anisotropy per bonding electron is greater in LiH, our calculations for LiH crystals predict that anisotropies measured in LiH will be smaller in magnitude than those in LiF. This is because the MSC-SRP for LiF have six electrons in 4σ -like orbitals while the MSC-SRP for LiH has only two electrons available to build resonant covalent bonds between any Li and its nearest neighbor H atoms.

V. APPLICATION TO OTHER ALKALI HALIDES

We have also applied the MSC-SRP method developed in Chapter 2 to other alkali halides. In Table 5 we show the alkali halides studied, the internuclear separation at which the Compton profile anisotropies were calculated,⁽¹⁵⁾ the actual crystal separation,⁽³⁰⁾ and the fractional ionic character⁽³¹⁾ of each of the molecules. Aside from LiF there are no experimental anisotropies available for comparison to our results.

In all of the alkali halides studied, the major contribution to the anisotropies came from the outermost MO's, i.e., the two least-bound sigma MO's and the least-bound pi MO. This is expected since the more tightly-bound, closed-shell MO's are not appreciably perturbed from their spherically-symmetric states and thus yield negligible anisotropies. Polarization effects are most evident in the anisotropies due to the next least-tightly bound sigma MO which corresponds to the valence s-electron in the halide atom. The outermost sigma orbital is the bonding orbital and is thus most affected by the molecular and crystalline environments. As expected it is this MO that determines the character of the total anisotropy. Total anisotropies, i.e., contributions from all the MO's are included, are plotted in Figs. 14-16.

A. Molecular Anisotropies.

The J_0 - J_{90} anisotropy for the alkali halide molecules is plotted in Fig. 14. As stated in Chapter 4 this anisotropy

TABLE V
CHARACTERISTICS OF THE ALKALI HALIDES ANALYZED BY
MSC - SRP

ALKALI HALIDE	(a) MOLECULAR SEPARATION (a.u.)	(b) ACTUAL CRYSTAL SEPARATION (a.u.)	(c) FRACTIONAL IONICITY (f)
LiF	3.55	3.806	.840
LiCl	4.55	4.857	.815
LiBr	4.85	5.199	.795
NaF	4.35	4.378	.888
NaCl	5.00	5.329	.863
KF	4.80	5.053	.933
KCl	5.65	5.947	.908

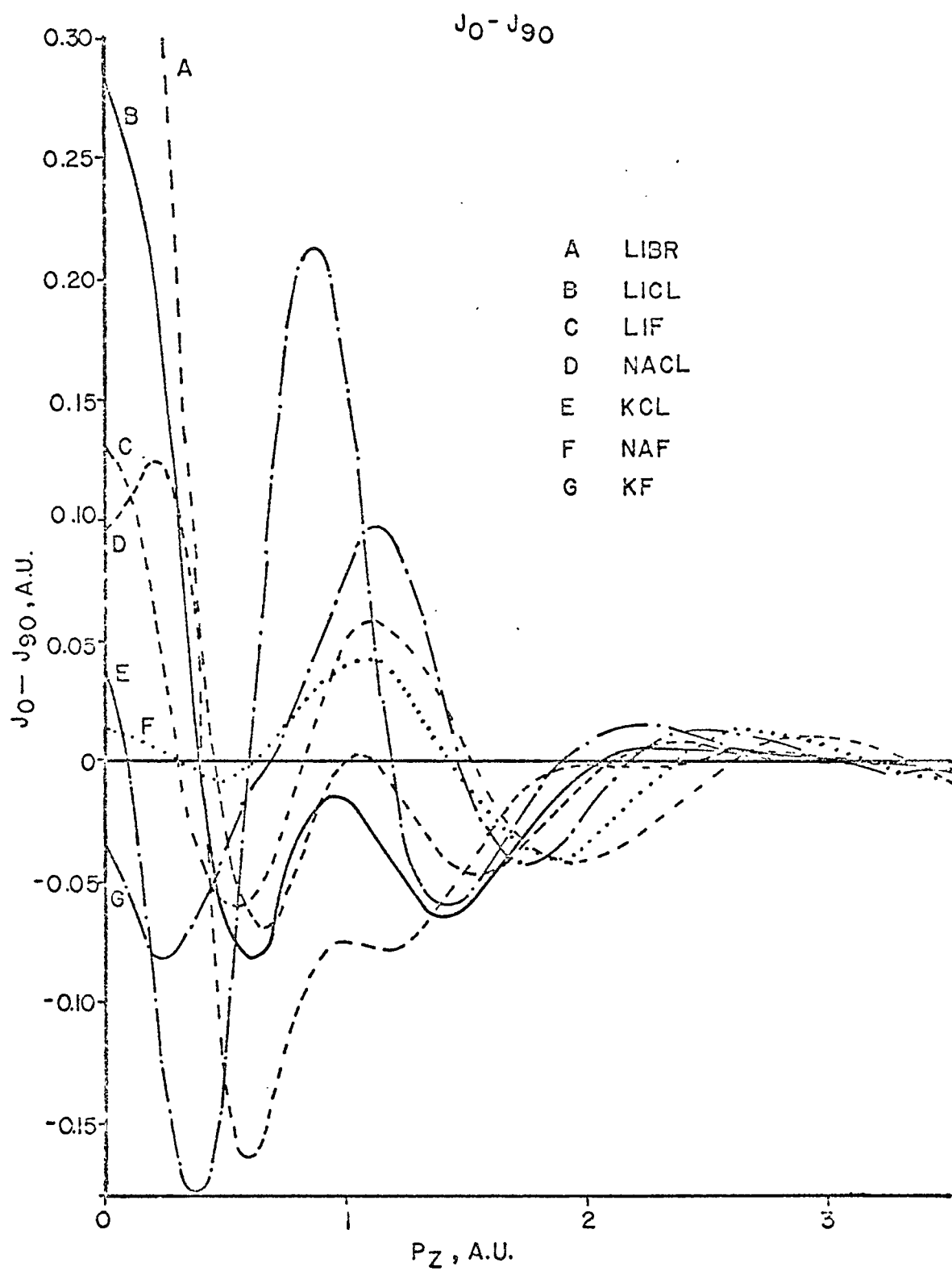
(a) reference 15

(b) reference 30

(c) reference 31

FIGURE 14

The $J_0 - J_{90}$ anisotropy in the alkali halides;
all curves were calculated at an internuclear
separation given by the second column in Table V.



is the difference in the Compton profiles with the scattering axis parallel and normal to the molecular bond. There are some trends in these anisotropies that may be related to the polarity, size, and ionic character of these molecules.

The magnitude of $J_0 - J_{90}$ at $p_z = 0$ has been discussed in some detail for LiF and LiH in the previous chapter. As mentioned in Chapter 4 this anisotropy becomes more positive as the alkali halide becomes more covalent. We may also view this as an increasing shift from p_z - to s-character in the bonding sigma MO as the molecule becomes more covalent; this is probably a good measure of the charge shared in the bond. The trend discussed above is most evident in the LiF, LiCl, LiBr sequence in which the molecule becomes more covalent. However NaF $\rightarrow$ NaCl are reversed in this plot and KF is negative so a complete generalization may not be truly possible.

The position and the spacing of the crossing-points in the $J_0 - J_{90}$ anisotropy are very sensitive functions of the internuclear separation of the atoms. As shown in Appendix C for the simple case of two s-STO's the term in the momentum density that leads to the anisotropies is proportional to $\cos(\vec{p} \cdot \vec{R})$ (eq. C-4). Thus, the larger R becomes, the closer are the spacings in the crossing-points and the peaks of the anisotropy. This is clearly evident in the LiF $\rightarrow$ LiBr sequence where R is getting bigger.

The extent of the $J_0 - J_{90}$ anisotropy, although sensitive to the value of R used in the calculation, may also

indicate the ionic or covalent character of the molecule. Again, consider the $\text{LiF} \rightarrow \text{LiBr}$ sequence. All three curves start at some positive value then oscillate about the horizontal. Note that the LiF anisotropy is damped out most slowly followed by LiCl then LiBr. This indicates that the valence MO's in LiBr are the most localized in momentum space and therefore the least localized in position space among the three molecules; this is true since the outer MO's of LiBr are the least tightly bound. Of course the value of R is not the same in all three molecules. Consider then two molecules with approximately the same R (see Table 6), e.g., LiBr and KF. From Table 6 we see that KF is about 93% ionic and LiBr about 80% ionic. In Fig. 14 note that KF exhibits appreciable anisotropy even at $p_z = 3.5$ a.u. while the anisotropy in LiBr is negligible beyond $p_z = 2.5$ a.u. It seems that the more ionic the molecule the less localized are the electrons in momentum space and the more spread out the J_0 - J_{90} anisotropy.

B. Crystalline Anisotropies

In Figures 15-16 and Tables 6-7 the MSC-SRP results for J_{100} - J_{110} and J_{100} are shown. Since these crystal anisotropies involve two more angles than J_0 - J_{90} (see Eqs. II-27a and II-27b), trends in these anisotropies may be harder to explain.

The spreading out of the anisotropy in the molecule as it becomes more ionic and thus less covalent seems to apply

FIGURE 15

MSC-SRP results for the 100 - 110 anisotropy
in the alkali halides.

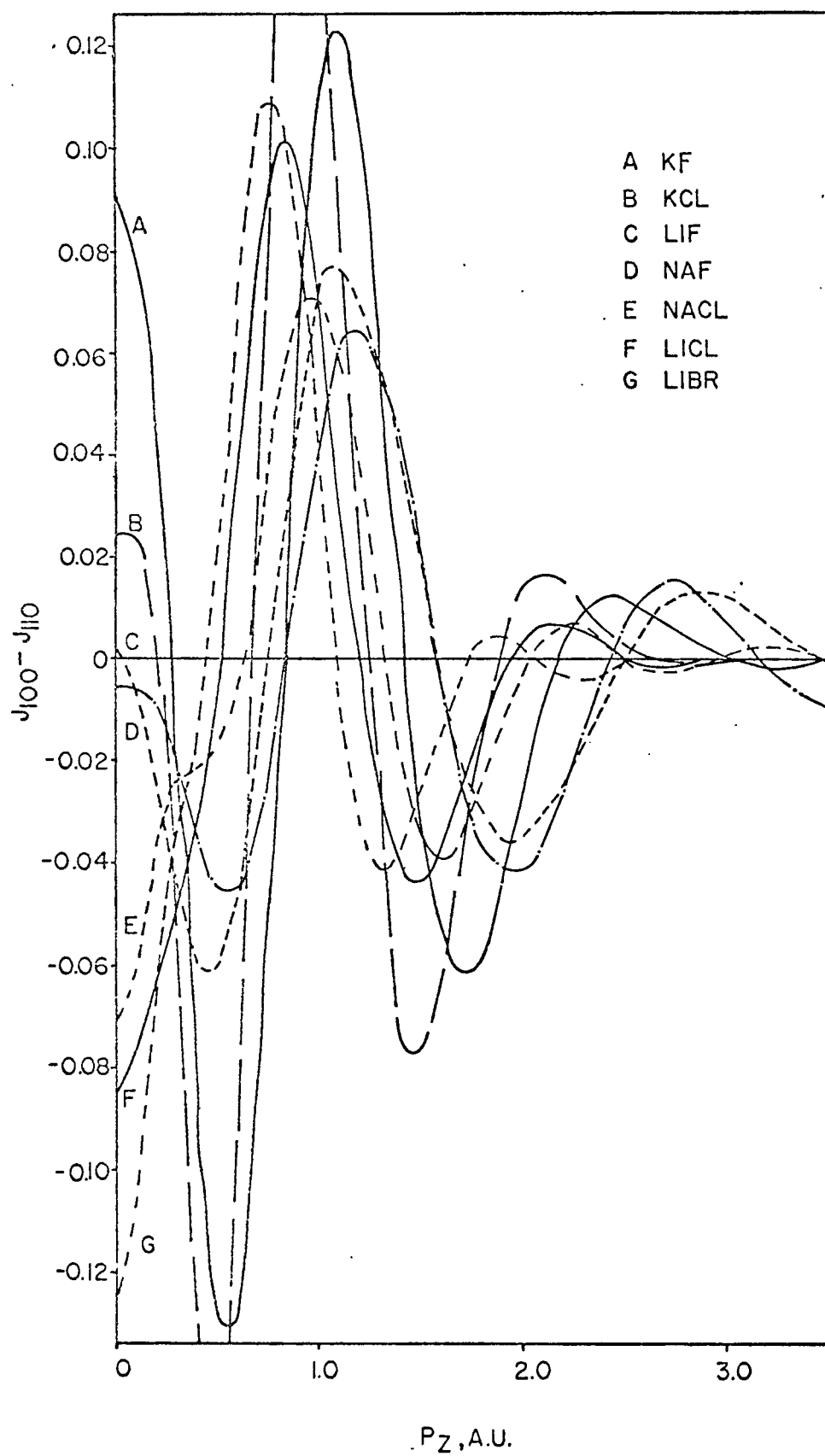


TABLE VI

MSC-SRP RESULTS FOR J_{100} - J_{110} ANISOTROPY OF THE ALKALI HALIDES

P_z , a.u.	LiF	LiCl	LiBr	NaF	NaCl	KF	KCl
.0	.0015	-.0849	-.1242	-.0063	-.0700	.0921	.0242
.1	-.0046	-.0779	-.1026	-.0058	-.0597	.0799	.0244
.2	-.0215	-.0625	-.0618	-.0087	-.0384	.0433	.0060
.3	-.0423	-.0480	-.0343	-.0187	-.0243	-.0167	-.0546
.4	-.0577	-.0339	-.0135	-.0335	-.0218	-.0826	-.1264
.5	-.0605	-.0084	.0206	-.0451	-.0177	-.1269	-.1478
.6	-.0467	.0307	.0671	-.0458	-.0048	-.1285	-.0876
.7	-.0185	.0715	.1029	-.0330	.0203	-.0873	.0242
.8	.0154	.0968	.1081	-.0093	.0483	-.0194	.1272
.9	.0462	.0969	.0820	.0182	.0670	.0515	.1762
1.0	.0677	.0740	.0393	.0427	.0713	.1031	.1598
1.2	.0715	.0025	-.0307	.0637	.0353	.1083	.0222
1.4	.0379	-.0400	-.0385	.0411	-.0180	.0206	-.0726
1.6	-.0032	-.0363	-.0141	-.0027	-.0390	-.0506	-.0626
1.8	-.0299	-.0137	.0017	-.0349	-.0257	-.0577	-.0138
2.0	-.0354	.0028	.0019	-.0409	-.0035	-.0266	.0132
2.2	-.0253	.0055	-.0037	-.0251	.0058	.0022	.0136
2.4	-.0091	.0017	-.0038	-.0027	.0030	.0124	.0052
2.6	.0049	-.0010	.0009	.0124	-.0015	.0093	-.0006
2.8	.0019	-.0007	.0046	.0149	-.0021	.0039	-.0022
3.0	.0115	.0007	.0036	.0077	.0001	.0007	-.0008
3.2	.0068	.0006	-.0001	-.0015	.0017	-.0012	-.0004
3.4	.0011	-.0007	-.0031	-.0076	.0009	-.0020	0
3.6	-.0037	-.0018	-.0029	-.0081	-.0021	-.0023	-.0004

FIGURE 16

MSC-SRP results for the 100-111 anisotropy
of the alkali halides.

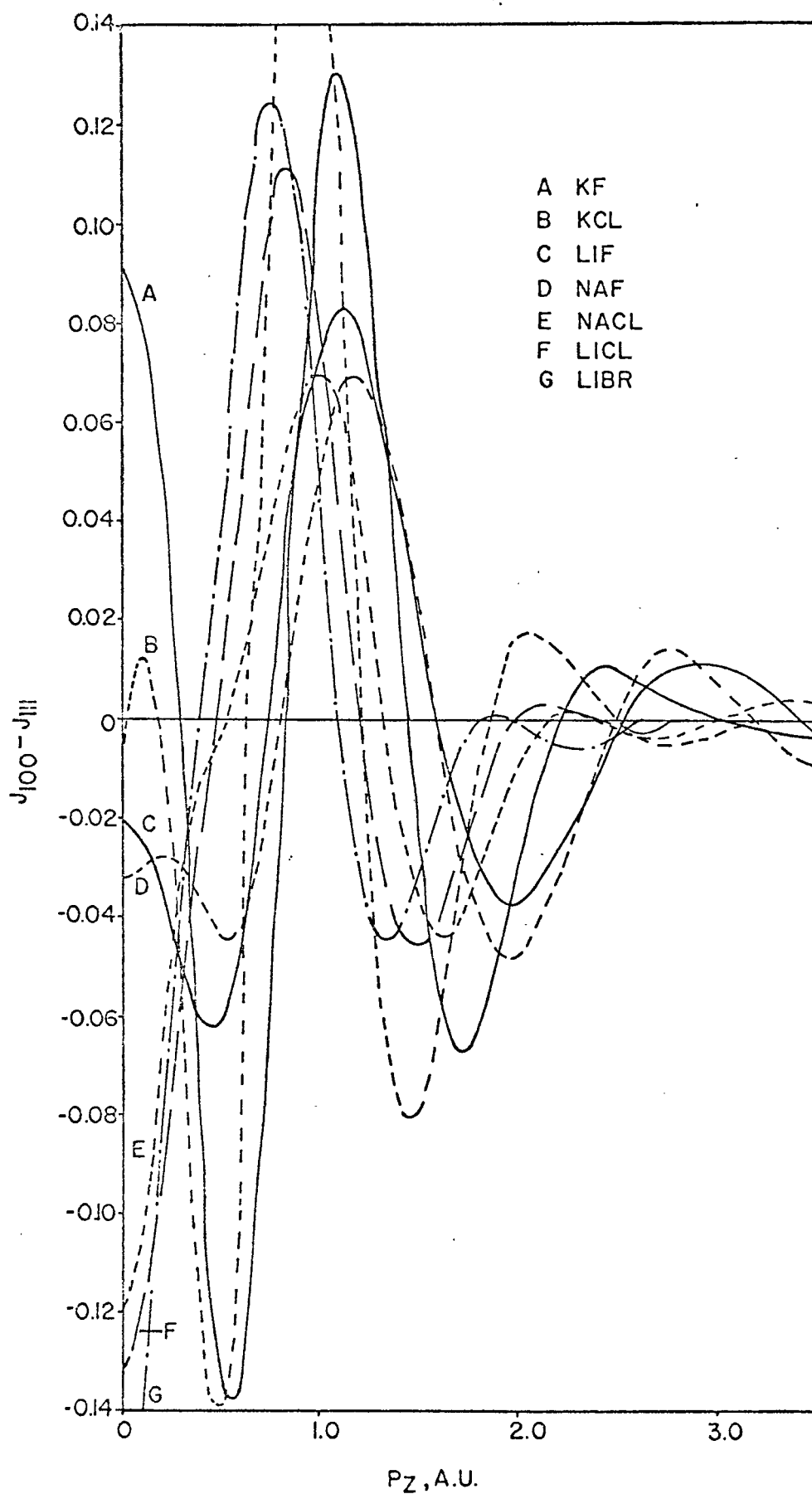


TABLE VII

MSC-SRP RESULTS FOR J_{100} - J_{111} ANISOTROPY OF THE ALKALI HALIDES

P_z , a.u.	LiF	LiCl	LiBr	NaF	NaCl	KF	KCl
.0	-.0207	-.1322	-.1811	-.0318	-.1187	.0907	-.0048
.1	-.0248	-.1176	-.1472	-.0296	-.1000	.0779	.0115
.2	-.0375	-.0843	-.0800	-.0275	-.0599	.0398	-.0055
.3	-.0515	-.0494	-.0277	-.0304	-.0256	-.0229	-.0544
.4	-.0611	-.0218	.0051	-.0379	-.0105	-.0904	-.1200
.5	-.0596	.0085	.0431	-.0435	-.0017	-.1342	-.1385
.6	-.0421	.0473	.0878	-.0401	.0102	-.1314	-.0768
.7	-.0121	.0863	.1204	-.0247	.0326	-.0847	.0356
.8	.0234	.1087	.1209	-.0009	.0585	-.0123	.1372
.9	.0549	.1056	.0900	.0263	.0754	.0613	.1825
1.0	.0753	.0799	.0427	.0511	.0775	.1123	.1608
1.2	.0772	.0029	-.0323	.0684	.0370	.1119	.0162
1.4	.0403	-.0419	-.0414	.0419	-.0195	.0185	-.0781
1.6	-.0030	-.0390	-.0170	-.0050	-.0429	-.0557	-.0629
1.8	-.0311	-.0173	-.0012	-.0401	-.0307	-.0623	-.0112
2.0	-.0371	-.0002	-.0008	-.0469	-.0087	-.0301	.0159
2.2	-.0267	.0026	-.0055	-.0309	.0014	-.0008	.0145
2.4	-.0101	-.0006	-.0047	-.0079	-.0007	.0103	.0039
2.6	.0043	-.0025	.0005	.0089	-.0032	.0071	-.0034
2.8	.0113	-.0017	.0051	.0130	-.0028	.0019	-.0049
3.0	.0109	.0003	.0045	.0070	.0001	-.0006	-.0026
3.2	.0064	.0005	.0002	-.0015	.0016	-.0014	-.0003
3.4	.0007	-.0009	-.0027	-.0076	.0004	-.0027	.0004
3.6	-.0034	-.0017	-.0027	-.0081	-.0014	-.0021	0

also to the crystalline anisotropies. This is evident in Figs. 15-16 where the more ionic crystals like KF and KCl exhibit relatively large anisotropies even at $p_z = 3.5$ a.u. while the more covalent LiBr crystal has practically zero anisotropy beyond $p_z = 2.5$ a.u.

The position and the spacing of the anisotropies are again largely a function of R . However, as we found out in the molecular case, the crossing points in KF are more spreadout than LiBr although they have the same R . Thus, even in the crystal it seems that the less ionic the crystal (e.g., LiBr) the more localized are its wavefunctions in momentum space and the closer are the crossing points.

The magnitude of the crystal anisotropies at $p_z = 0$ for these alkali halides is harder to explain than the J_0-J_{90} anisotropy. The complexity of these anisotropies should be evident from Eq. (II-27). It is interesting to note that the anisotropy at $p_z = 0$ seems to become more negative as the crystal becomes less ionic; this is true in all cases except LiF. Whether this trend is still there at the correct crystal spacing remains to be seen since MO's at these values of R are not presently available.

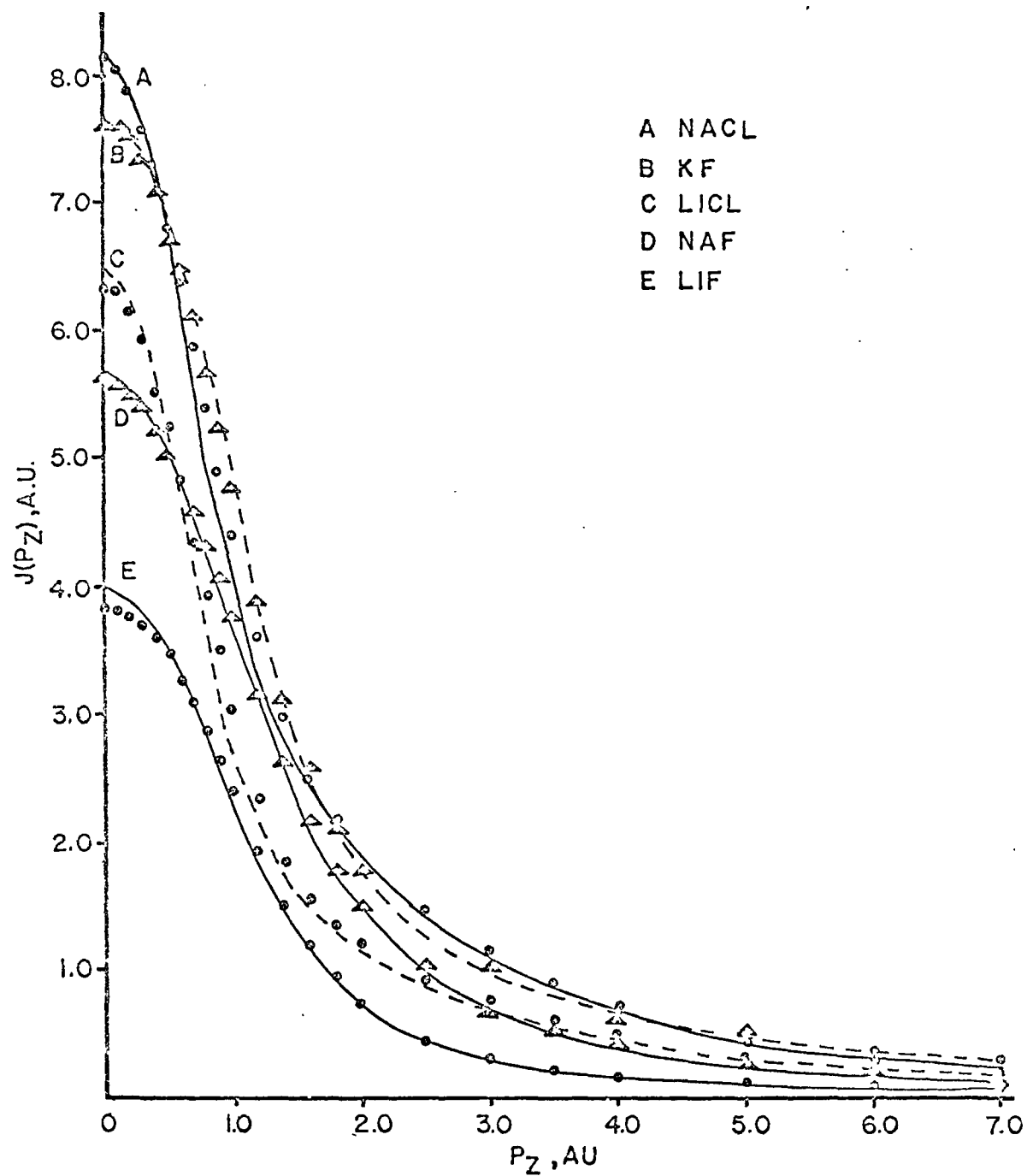
C. Total Compton Profiles.

In Figure 17 we show the results of the MSC-SRP calculation for the averaged total Compton profile (Eq. II-28) for some of the alkali halides. The experimental results⁽³²⁾ on polycrystalline (isotropic) samples are also indicated.

FIGURE 17

MSC-SRP results for the average total Compton profiles of the alkali halides. The experimental results on polycrystalline samples (Ref. 32) are indicated as circles or triangles.

MSC-SRP AVERAGED COMPTON PROFILE FOR
ALKALI HALIDE CRYSTALS AND EXPT. RESULTS



Each of the Compton profiles is normalized to the total number of electrons in the diatomic. Thus, LiF is normalized to 12 electrons while NaF is normalized to 20 electrons.

Taking into consideration the multiple scattering and resolution corrections that must be made on the data the MSC-SRP results are all in good agreement with the experiment. It is interesting to note that MSC-SRP is consistently higher than the experiment at very low p_z . This is expected since solid-state effects not accounted for by the nearest neighbor approximation inherent in MSC-SRP should tend to localize the electrons more in position space and thus spread out the Compton profiles to higher p_z and decrease them at low p_z .

VI. CONCLUSION

What are the implications of these calculations? First of all, as pointed out by Berggre, Martino, Eisenberger and Reed, (9) the most recent conclusion known from an analysis of elastic X-ray scattering measurements (33,34) that the charge density is spherically symmetric about each ion (35) is incorrect. That they are anisotropic is evident from Compton profile measurements and from our calculations. Furthermore the fact that we have obtained good agreement with experiment by modeling a crystal using bonds closely related to those in the diatomic molecule implies that the bond polarity and covalency on the crystal and the partial charges on each ion are nearly the same as in the diatomic molecule. (14,36)

What are the advantages of our method over alternate theoretical approaches? First of all, we obtain a clear indication of the influence of various molecular orbitals and localized bonds on the Compton profile anisotropies. Our calculations coupled with perturbation theory and with Compton measurements should constitute a reliable method for analyzing charge distributions in crystals.

A second advantage is the fact that our approach preserves the nature of molecular bonds. Thus we expect it to be superior to other approaches in predicting anisotropies in more covalently bonded crystals such as diamond and LiH. There is some evidence that this will be the case. For example Snyder and coworkers⁽¹²⁾ were able to obtain the right number of crossings in anisotropies between Compton profiles

parallel and perpendicular to the C_6 axis for crystalline graphite by modeling a carbon atom on a fragment obtained from a selected piece of a butadiene molecule. In fact, the anisotropy curve predicted by this simple model was closer to the experimental curve than that obtained using the pseudo potential or OPW approach.(13)

Ab initio calculations on LiF dimers and LiF chains should be made to further substantiate some of the hypotheses made in this work. The effects of anisotropies due to next-nearest neighbors should also be investigated. The method can be extended to body-centered-cubic (BCC) crystals but the symmetrization of the MO's might not be as evident as in the FCC case.

The MSC-SRP approach should provide a fresh approach to the study of more covalent diatomic molecules like the hydrides and more covalent FCC crystals like MgO.

In Chapter. 1 we found that the Compton profile is obtained from the momentum density distribution through the double integral (see eq. II-8)

$$J(p_z') = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dp_x' dp_y' \rho(p_x', p_y', p_z') \quad (\text{A-1})$$

From the expression for ρ (eq. II-23) it is clear that analytical solutions to eq. (A-1) will not be easy to obtain. However by a suitable change of variables eq. (A-1) can be easily transformed to an integral solvable by the Gauss-Legendre quadrature method.

In any quadrature solution the function to be integrated is approximated by a polynomial (Hermite, Laguerre, Legendre, etc.) that is well-defined in the region of integration and which converges fast enough so that computer time is kept to a minimum. Since Legendre polynomials are defined only in the interval $[-1, +1]$ we need a change of variables for the infinite integrals in eq. (A-1).

First, consider the single integral

$$\int_{-\infty}^{\infty} dx f(x) \quad (\text{A-2})$$

By the change of variables $X = -\log\left(\frac{x'+1}{2}\right)$ in the interval $[0, \infty]$ and $X = +\log\left(\frac{x'+1}{2}\right)$ in the interval $[-\infty, 0]$ the limits are changed to $[-1, +1]$ and the integral takes the form

$$\int_{-\infty}^{\infty} f(x) dx = \int_{-1}^{+1} \frac{f(\log \frac{x'+1}{2}) + f(-\log \frac{x'+1}{2})}{x'+1} dx' \quad (\text{A-3})$$

The right-hand side of equation (A-3) is now in a form suitable for Gauss-Legendre quadrature.

If we let x_i represent the i th root of the approximate N -th order Legendre polynomial, $P_N(x)$, and w_i the corresponding weight factor, the integral is transformed to a sum over these N terms,

$$\int_{-\infty}^{\infty} f(x) dx = \sum_{i=1}^N w_i \frac{f(\log \frac{x_{i+1}}{2}) + f(-\log \frac{x_{i+1}}{2})}{x_{i+1}} \quad (\text{A-4})$$

These weights and roots are tabulated, for example, in Abramowitz and Stegun. (38)

This result, eq. (A-4), may easily be extended to a double integral, thus,

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) dx dy &= \sum_{i=1}^N \sum_{j=1}^N w_i w_j (x_{i+1})^{-1} (y_{j+1})^{-1} \times \\ &\quad \left[f\left(\log \frac{x_{i+1}}{2}, \log \frac{y_{j+1}}{2}\right) + f\left(-\log \frac{x_{i+1}}{2}, \log \frac{y_{j+1}}{2}\right) \right. \\ &\quad \left. + f\left(\log \frac{x_{i+1}}{2}, -\log \frac{y_{j+1}}{2}\right) + f\left(-\log \frac{x_{i+1}}{2}, -\log \frac{y_{j+1}}{2}\right) \right] \quad (\text{A-5}) \end{aligned}$$

Equation (A-5) is used in evaluating eq. (A-1) with appropriate simplifications due to the symmetry of ρ .

APPENDIX B

MOMENTUM TRANSFORM OF A 3d STO

As an example of the use of the recursion relations (Eqs. II-17 to II-19) let us calculate the momentum transform of a 3d STO. For a 3d STO we set $n = 3$ and $l = 2$ in equation (II-16),

$$\chi_{3d}^{STO}(\vec{p}) = (-i)^2 \sqrt{\frac{2}{\pi}} k_3 \left[\int_0^\infty dr r^4 e^{-\mathcal{I}r} j_2(pr) \right] Y_2^m(\hat{p}) \quad (B-1)$$

where $k_3 = (2\mathcal{I})^{7/2} (6!)^{-1/2}$. From equation (II-19)

$$j_2(pr) = 3 \frac{j_1(pr)}{pr} - j_0(pr) \quad (B-2)$$

so the radial integral in (B-1) becomes

$$\int_0^\infty dr r^4 e^{-\mathcal{I}r} j_2(pr) = \frac{3}{p} \int_0^\infty dr r^3 e^{-\mathcal{I}r} j_1(pr) - \int_0^\infty dr r^4 e^{-\mathcal{I}r} j_0(pr) \quad (B-3)$$

By equation (II-18) the first integral on the right is given by

$$\begin{aligned} \int_0^\infty dr r^3 e^{-\mathcal{I}r} j_1(pr) &= -\frac{d}{d\mathcal{I}} \left(\frac{2p}{(\mathcal{I}^2 + p^2)^2} \right) \\ &= \frac{8\mathcal{I}p}{(\mathcal{I}^2 + p^2)^3} \end{aligned} \quad (B-4)$$

and from equation (II-17)

$$\begin{aligned} \int_0^\infty dr r^4 e^{-\mathcal{I}r} j_0(pr) &= \left(-\frac{d}{d\mathcal{I}} \right)^2 \left(\frac{1}{\mathcal{I}^2 + p^2} \right) \\ &= \frac{24(\mathcal{I}^3 - \mathcal{I}p^2)}{(\mathcal{I}^2 + p^2)^4} \end{aligned} \quad (B-5)$$

Substituting (B-4) and (B-5) in (B-3) we obtain

$$\int_0^{\infty} dr r^4 e^{-\mathfrak{f}r} j_2(pr) = \frac{48 \mathfrak{f} p^2}{(\mathfrak{f}^2 + p^2)^4} \quad (\text{B-6})$$

From (B-6) and the expression for k_3 we get the final result

$$\chi_{3d}^{sto}(\vec{p}) = -\sqrt{\frac{16 \mathfrak{f}^7}{45 \pi}} \frac{48 \mathfrak{f} p^2}{(\mathfrak{f}^2 + p^2)^4} Y_2^m(\hat{p}) \quad (\text{B-7})$$

APPENDIX C OVERLAP TERM IN THE MOMENTUM DENSITY

We have shown that the momentum wavefunction for a diatomic molecule may be written as (Eq. II-12)

$$\chi_i(\vec{p}) = \chi_i^A(\vec{p}) + e^{-i\vec{p}\cdot\vec{R}} \chi_i^B(\vec{p}) \quad (C-1)$$

where $\chi_i^{A,B}$ are the STO's centered on atoms A and B, respectively. The momentum density for the *i*th MO is then

$$\rho_i(\vec{p}) = |\chi_i(\vec{p})|^2 = |\chi_i^A(\vec{p}) + e^{-i\vec{p}\cdot\vec{R}} \chi_i^B(\vec{p})|^2 \quad (C-2)$$

which is easily shown to be

$$\rho_i(\vec{p}) = |\chi_i^A(\vec{p})|^2 + |\chi_i^B(\vec{p})|^2 + 2 \operatorname{Re}(\chi_i^A \chi_i^{B*} e^{i\vec{p}\cdot\vec{R}}) \quad (C-3)$$

The first two terms are the momentum densities due to the STO's centered on each atom and the third term is what we shall call the overlap term in the momentum density.

Let us consider χ_i^A, χ_i^B to be s-type STO's. Since s-type STO's are spherically symmetric the anisotropy in the momentum density would be purely associated with the overlap term, i.e.,

$$\rho_{ov}(\vec{p}) = 2 \chi_i^A(p) \chi_i^B(p) \cos(\vec{p}\cdot\vec{R}) \quad (C-4)$$

In this simple case we clearly see the oscillatory character in the density as a function of $\vec{p} \cdot \vec{R}$.

In the actual MO's we used in this work, it is also possible to break down the anisotropies into the different overlap contributions and find out their effect on the total anisotropy, but this is in general a tedious affair when you have 40 STO's as a basis set.

APPENDIX D

COMPUTER PROGRAMS

The calculation of the MSC-SRP crystalline anisotropies involves two steps: first, the molecular Compton profiles for each MO of the diatomic are calculated and stored in a file; second, from the data on this file for the different MO's the required anisotropies are then computed with the proper occupation numbers of each MO being accounted for.

The MAIN program reads in the MO data and calculates the Compton profiles through a FUNCTION subprogram CHISQ which calculates the momentum density as a sum of the constituent STO densities. The auxiliary program ANIS then completes the calculation of the anisotropies and the average Compton profile.

```

1 C *****
2 C THIS IS THE MAIN PROGRAM THAT WILL CALCULATE THE COMPTON PROFILE
3 C FOR EACH MOLECULAR ORBITAL FOR ANY DIATOMIC MOLECULE. THIS WILL
4 C BE DONE FOR DIFFERENT ANGLES TO SEE THE ANISOTROPY IN THE
5 C PROFILES. GAUSS-LEGENDRE QUADRATURE WILL BE USED IN THE DOUBLE
6 C INTEGRATION. THIS PROGRAM CALLS FUNCTION CHISO WHICH EVALUATES
7 C THE MOMENTUM DENSITY OF EACH MO ON A PLANE .
8 C *****
9 DATA PI/3.141592651/
10 C W( ) IS THE ARRAY OF WEIGHTS AND Z( ) THE ROOTS FOR THE
11 C GAUSSIAN INTEGRATION. ANGLE IS THE ARRAY OF ANGLES NEEDED.
12 C PZ IS THE ARRAY OF PZ'S AT WHICH J(PZ) IS CALCULATED.
13 DIMENSION ANGLE(10),PZ(100)
14 DOUBLE PRECISION COL1(100),COL2(100),COL3(100),COL4(100)
15 *,COL5(100)
16 DOUBLE PRECISION W(100),Z(100)
17 DOUBLE PRECISION XX,YY,ZZ1,FUN,SUM1,PZZ,CHISO
18 C COMMON STATEMENTS
19 C ALPHA IS THE ANGLE AT WHICH J(PZ) IS CALCULATED
20 C RAD IS THE DISTANCE IN AU BETWEEN ATOMS A AND B
21 C NTYPE=1 MEANS SIGMA ORBITAL, =2 MEANS PI ORBITAL
22 COMMON ALPHA,PAD,NTYPE
23 C N1S,C1S( ),G1S( ) REFER TO THE NUMBER OF 1S STO'S ON ATOM A,
24 C C1S IS THE ARRAY OF COEFFICIENTS, AND G1S THE ARRAY OF
25 C EXPONENTS FOR THIS STO.IT IS ASSUMED THAT ONLY 1S-4S,
26 C 2P-4P, 3D, AND 4F STO'S ARE USED IN THE BASIS SET OF THE MO.
27 C M1S,D1S AND H1S REFER TO PARAMETERS FOR 1S ON ATOM B
28 COMMON N1S,C1S(5),G1S(5),N2S,C2S(5),G2S(5),N3S,C3S(5),G3S(5)
29 COMMON N4S,C4S(5),G4S(5),N2P,C2P(5),G2P(5),N3P,C3P(5),G3P(5)
30 COMMON N4P,C4P(5),G4P(5),N3D,C3D(5),G3D(5),N4F,C4F(5),G4F(5)
31 COMMON M1S,D1S(5),H1S(5),M2S,D2S(5),H2S(5),M3S,D3S(5),H3S(5)
32 COMMON M4S,D4S(5),H4S(5),M2P,D2P(5),H2P(5),M3P,D3P(5),H3P(5)
33 COMMON M4P,D4P(5),H4P(5),M3D,D3D(5),H3D(5),M4F,D4F(5),H4F(5)
34 C SET UP THE ARRAY FOR GAUSS-LEGENDRE QUADRATURE. NW=NUMBER
35 C OF ROOTS REQUIRED FOR THE INTEGRAL.ONLY THE POSITIVE ROOTS ARE READ
36 C IN .AND THEIR CORRESPONDING WEIGHTS. THESE ARE FOUND IN ABRAMOWITZ
37 C AND STEGUN.
38 READ 100,NW
39 100 FORMAT ( )
40 NW=NW/2
41 READ 100,(W(I),I=1,NW),(Z(I),I=1,NW)
42 C THE NEGATIVE ROOTS HAVE THE SAME WEIGHTS AS THE POSITIVE SO
43 DO 88 I=1,NW
44 W(I+NW)=W(I)
45 88 Z(I+NW)=-Z(I)
46 C READ THE PZ ARRAY
47 READ 100,NPZ,(PZ(I),I=1,NPZ)
48 C READ THE ANGLE ARRAY IN DEGREES
49 C FOR AN FCC CRYSTAL WE NEED 0,45,55,AND 90 DEGREES PROFILES.
50 READ 100,NANG,(ANGLE(I),I=1,NANG)
51 C THE NAME OF THE MOLECULE
52 READ 101,TITLE1
53 101 FORMAT(A6)
54 C THE SEPARATION BETWEEN ATOMS IN AU'S
55 READ 100,RAD
56 C NSIG AND NPI WILL COUNT THE NUMBER OF SIGMA AND PI ORBITALS
57 C IF EITHER IS GREATER THAN 1 ONLY THE COEFFICIENTS OF THE NEXT

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58      C MO WILL BE READ.
59          NSIG=0
60          NPI=0
61      C READ THE TYPE OF MOLECULAR ORBITAL
62      1      READ (5,100,END=99) NTYPE
63      C TYPE OF MOLECULAR ORBITAL
64          READ 101,TITLE2
65          IF (NTYPE.EQ.1)NSIG=NSIG+1
66          IF(NTYPE.EQ.2)NPI=NPI+1
67          IF(NSIG.GT.1.AND.NPI.EQ.0)GO TO 2
68          IF(NPI.GT.1)GO TO 2
69      C READ THE EXPONENTS FOR SIGMA AND PI MO'S
70          READ 100,
71          *N1S,(G1S(I),I=1,N1S),N2S,(G2S(I),I=1,N2S),
72          *N3S,(G3S(I),I=1,N3S),N4S,(G4S(I),I=1,N4S),
73          *N2P,(G2P(I),I=1,N2P),N3P,(G3P(I),I=1,N3P),
74          *N4P,(G4P(I),I=1,N4P),N3D,(G3D(I),I=1,N3D),
75          *N4F,(G4F(I),I=1,N4F),
76          *M1S,(H1S(I),I=1,M1S),M2S,(H2S(I),I=1,M2S),
77          *M3S,(H3S(I),I=1,M3S),M4S,(H4S(I),I=1,M4S),
78          *M2P,(H2P(I),I=1,M2P),M3P,(H3P(I),I=1,M3P),
79          *M4P,(H4P(I),I=1,M4P),M3D,(H3D(I),I=1,M3D),
80          *M4F,(H4F(I),I=1,M4F)
81      C NOW READ THE COEFFICIENTS OF THE STF'S
82      2      READ 100,
83          *N1S,(C1S(I),I=1,N1S),N2S,(C2S(I),I=1,N2S),
84          *N3S,(C3S(I),I=1,N3S),N4S,(C4S(I),I=1,N4S),
85          *N2P,(C2P(I),I=1,N2P),N3P,(C3P(I),I=1,N3P),
86          *N4P,(C4P(I),I=1,N4P),N3D,(C3D(I),I=1,N3D),
87          *N4F,(C4F(I),I=1,N4F),
88          *M1S,(D1S(I),I=1,M1S),M2S,(D2S(I),I=1,M2S),
89          *M3S,(D3S(I),I=1,M3S),M4S,(D4S(I),I=1,M4S),
90          *M2P,(D2P(I),I=1,M2P),M3P,(D3P(I),I=1,M3P),
91          *M4P,(D4P(I),I=1,M4P),M3D,(D3D(I),I=1,M3D),
92          *M4F,(D4F(I),I=1,M4F)
93      C PRINT THE STF PARAMETERS
94          PRINT 103
95      103      FORMAT('1',1X,'THE STF COEFFICIENTS AND EXPONENTS'//)
96          PRINT 100,N1S,(C1S(I),I=1,N1S),(G1S(I),I=1,N1S)
97          PRINT 100,N2S,(C2S(I),I=1,N2S),(G2S(I),I=1,N2S)
98          PRINT 100,N3S,(C3S(I),I=1,N3S),(G3S(I),I=1,N3S)
99          PRINT 100,N4S,(C4S(I),I=1,N4S),(G4S(I),I=1,N4S)
100         PRINT 100,N2P,(C2P(I),I=1,N2P),(G2P(I),I=1,N2P)
101         PRINT 100,N3P,(C3P(I),I=1,N3P),(G3P(I),I=1,N3P)
102         PRINT 100,N4P,(C4P(I),I=1,N4P),(G4P(I),I=1,N4P)
103         PRINT 100,N3D,(C3D(I),I=1,N3D),(G3D(I),I=1,N3D)
104         PRINT 100,N4F,(C4F(I),I=1,N4F),(G4F(I),I=1,N4F)
105         PRINT 100,M1S,(D1S(I),I=1,M1S),(H1S(I),I=1,M1S)
106         PRINT 100,M2S,(D2S(I),I=1,M2S),(H2S(I),I=1,M2S)
107         PRINT 100,M3S,(D3S(I),I=1,M3S),(H3S(I),I=1,M3S)
108         PRINT 100,M4S,(D4S(I),I=1,M4S),(H4S(I),I=1,M4S)
109         PRINT 100,M2P,(D2P(I),I=1,M2P),(H2P(I),I=1,M2P)
110         PRINT 100,M3P,(D3P(I),I=1,M3P),(H3P(I),I=1,M3P)
111         PRINT 100,M4P,(D4P(I),I=1,M4P),(H4P(I),I=1,M4P)
112         PRINT 100,M3D,(D3D(I),I=1,M3D),(H3D(I),I=1,M3D)
113         PRINT 100,M4F,(D4F(I),I=1,M4F),(H4F(I),I=1,M4F)
114      C PRINT THE HEADER
115          PRINT 104,TITLE1,RAD, TITLE2

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116 104 FORMAT('1',//,1X,'DIATOMIC MOLECULE = ',A6,/,
117 *1X'EQUILIBRIUM SEPARATION = ',F12.6,' AU',/,
118 *1X,'COMPTON PROFILE FOR THE ',A6,' ORBITAL',/)
119 C NOW DO THE INTEGRATION
120 C THIS DO WILL READ THE ALPHA NEEDED FOR THE INTEGRATION
121 C NANG =NO. OF ANGLES AT WHICH C. P. IS NEEDED.
122 C IF NANG=4 IT'S AN FCC CRYSTAL,IF =5 BCC.
123 DO 1001 K=1,NANG
124 ALPHA=ANGLE(K)*PI/180.
125 C DO LOOP FOR DIFFERENT PZ'S IN J(PZ)
126 DO 1002 L=1,NPZ
127 PZZ=PZ(L)
128 C SUM1 WILL CONTAIN THE INTEGRAL DESIRED = J(PZ)
129 SUM1=0.000
130 C START OF THE INTEGRATION ROUTINE
131 C DO LOOP TO CALCULATE THE INTEGRAL BY GAUSS-LEGENDRE QUAD-
132 C RATURE. NW*NW TERMS ARE SUMMED
133 DO 1003 I=1,NW
134 C CHANGE VARIABLES TO MAKE LIMITS OF INTEGRATION (-1,1)
135 C DLOG IS DOUBLE PRECISION LOGARITHM
136 XX=DLOG((Z(I)+1.)/2.)
137 DO 1004 J=1,NW
138 YY=DLOG((Z(J)+1.)/2.)
139 C CALCULATE THE VALUE OF THE INTEGRAND
140 IF(K.EQ.1.OR.K.EQ.5)ZZ1=2*CHISQ(XX,YY,PZZ)
141 IF(K.EQ.4.AND.NANG.EQ.4)ZZ1=CHISQ(XX,YY,PZZ)*2
142 IF (K.EQ.4.AND.NANG.EQ.5)ZZ1=CHISQ(XX,YY,PZZ)+CHISQ(-XX,YY,PZ
143 IF(K.EQ.2.OR.K.EQ.3)ZZ1=CHISQ(XX,YY,PZZ)+CHISQ(-XX,YY,PZZ)
144 FUN=2.*W(I)*W(J)/(Z(I)+1.)/(Z(J)+1.)
145 1004 SUM1=SUM1+FUN*ZZ1
146 1003 CONTINUE
147 C THE INTEGRALS ARE STORED PER ANGLE FOR PRINTOUT LATER
148 IF(K.EQ.1) COL1(L)=SUM1
149 IF (K.EQ.2) COL2(L)=SUM1
150 IF(K.EQ.3)COL3(L)=SUM1
151 IF(K.EQ.4) COL4(L)=SUM1
152 IF(K.EQ.5) COL5(L)=SUM1
153 1002 CONTINUE
154 1001 CONTINUE
155 IF(NANG.EQ.5)GO TO 126
156 PRINT 125
157 125 FORMAT(1X,'PZ(AU)',5X,' J(0)',9X,'J(45)',7X,
158 *'J(54.7)',7X,'J(90)'/)
159 DO 122 I=1,NPZ
160 122 PRINT 110,PZ(I),COL1(I),COL2(I),COL3(I),COL4(I)
161 110 FORMAT(1X,F5.2,4(5X,F8.6))
162 C DATA IS ALSO PRINTED IN A FILE = 7 FOR FUTURE USE.
163 WRITE(7,111) TITLE1,TITLE2,RAD
164 111 FORMAT (A6,1X,A6,5X,'R=',F8.6)
165 WRITE(7,188) NPZ
166 188 FORMAT(I3)
167 DO 123 I=1,NPZ
168 123 WRITE (7,124) PZ(I),COL1(I),COL2(I),COL3(I),COL4(I)
169 124 FORMAT(F5.2,4(2X,F8.4))
170 GO TO 1
171 126 PRINT 127
172 127 FORMAT(1X,'PZ(AU)',5X,' J(0)',9X,'J(35.3)',7X,'J(45)',
173 *7X,'J(60)',7X,'J(90)'/)

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174      DO 128 I=1,NPZ
175      PRINT 116,PZ(I),COL1(I),COL2(I),COL3(I),COL4(I),COL5(I)
176      FORMAT(1X,F5.2,5(5X,F8.6))
177      C DATA IS ALSO PRINTED IN A FILE = 7 FOR FUTURE USE.
178      WRITE(7,111) TITLE1,TITLE2,RAD
179      WRITE(7,188) NPZ
180      DO 133 I=1,NPZ
181      133 WRITE(7,134) PZ(I),COL1(I),COL2(I),COL3(I),COL4(I),COL5(I)
182      134 FORMAT(F5.2,5(2X,F8.4))
183      GO TO 1
184      99  STOP
185      END

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1 C THIS IS A FUNCTION SUBPROGRAM THAT CALCULATES THE SQUARE OF THE
2 C MOLECULAR ORBITAL MOMENTUM WAVE FUNCTION FOR A DIATOMIC
3 C MOLECULE. THE POSITION WAVE FUNCTION IS A COMBINATION
4 C OF SLATER TYPE FUNCTIONS (STF) ON BOTH ATOMS.
5 C *****
6 C DEFINE THE FUNCTION CHISO
7 C DOUPLE PRECISION FUNCTION CHISO(PX, PY, PZ)
8 C DOUPLE PRECISION PI, XN1, XN2, XN3, XN4, R1S, R2S, R3S, R4S
9 C *, R2P, R3P, R4P, R3D, R4F, Y00, Y10, Y20, Y11, Y21, Y31,
10 C *RR, PI, P, X, PX, PY, PZ, PZR, A, RX, RY
11 C DATA PI/3.1415926535897932DC/
12 C DEFINE STATEMENT FUNCTIONS
13 C THE NORMALIZATION COEFFICIENTS
14 C XN1(G)=DSQRT(8.0*G**3/PI)
15 C XN2(G)=DSQRT(8*G**5/PI/3.)
16 C XN3(G)=DSQRT(16*G**7/45./PI)
17 C XN4(G)=DSQRT(8*G**9/315/PI)
18 C DEFINE THE RADIAL MOMENTUM FUNCTIONS
19 C THE S-TYPES
20 C R1S(P,G)=XN1(G)*2.0*G/(G**2+P**2)**2
21 C R2S(P,G)=XN2(G)*(6*G**2-2*P**2)/(G**2+P**2)**3
22 C R3S(P,G)=XN3(G)*24*(G**3-G*P**2)/(G**2+P**2)**4
23 C R4S(P,G)=XN4(G)*24*(5*G**4-10.*G**2*P**2+P**4)/(G**2+P**2)**5
24 C THE P-TYPES.
25 C R2P(P,G)=-XN2(G)*8*G*P/(G**2+P**2)**3
26 C R3P(P,G)=-XN3(G)*(40.*G**2*P-8*P**3)/(G**2+P**2)**4
27 C R4P(P,G)=-XN4(G)*(240*G**3*P-144*G*P**3)/(P**2+G**2)**5
28 C D-TYPE
29 C R3D(P,G)=-XN3(G)*48.*G*P**2/(G**2+P**2)**4
30 C F-TYPE
31 C R4F(P,G)=XN4(G)*384*G*P**3/(G**2+P**2)**5
32 C THE SPHERICAL HARMONICS W/O THE PHI DEPENDENCE
33 C Y00(X)=1./DSQRT(4.0*PI)+X*0.0
34 C Y10(X)=DSQRT(3./4./PI)*X
35 C Y20(X)=DSQRT(5./4./PI)*(1.5*X**2-.5)
36 C Y30(X)=DSQRT(7./4/PI)*(2.5*X**3-1.5*X)
37 C Y11(X)=-DSQRT(3./8/PI)*DSQRT(1-X**2)
38 C Y21(X)=-DSQRT(15./8/PI)*X*DSQRT(1-X**2)
39 C Y31(X)=-DSQRT(21./4/PI)*DSQRT(1-X**2)*(5*X**2-1)/4
40 C END OF FUNCTION STATEMENTS DEFINITION
41 C *****
42 C COMMON STATEMENTS
43 C ALPHA IS THE ANGLE AT WHICH J(PZ) IS CALCULATED
44 C RAD IS THE DISTANCE IN AU BETWEEN ATOMS A AND B
45 C NTYPE=1 MEANS SIGMA ORBITAL, =2 MEANS PI ORBITAL
46 C COMMON ALPHA, RAD, NTYPE
47 C N1S=NUMBER OF 1S STF ON ATOM A C1S(I)=1S STF COEFFICIENTS
48 C G1S(I)=1S STF EXPONENTS.
49 C OTHERS ARE SIMILARLY DEFINED.
50 C COMMON A1S, C1S(5), G1S(5), N2S, C2S(5), G2S(5), N3S, C3S(5), G3S(5)
51 C COMMON N4S, C4S(5), G4S(5), N2P, C2P(5), G2P(5), N3P, C3P(5), G3P(5)
52 C COMMON N4P, C4P(5), G4P(5), N3D, C3D(5), G3D(5), N4F, C4F(5), G4F(5)
53 C M1S, D1S, H1S ARE DEFINED AS BEFORE BUT FOR ATOM B
54 C COMMON M1S, D1S(5), H1S(5), M2S, D2S(5), H2S(5), M3S, D3S(5), H3S(5)
55 C COMMON M4S, D4S(5), H4S(5), M2P, D2P(5), H2P(5), M3P, D3P(5), H3P(5)
56 C COMMON M4P, D4P(5), H4P(5), M3D, D3D(5), H3D(5), M4F, D4F(5), H4F(5)
57 C *****

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58 C RR WILL STORE THE REAL PART OF CHI
59 C RI WILL STORE THE IMAGINARY PART OF CHI
60 RR=C.000
61 RI=C.000
62 C THE MAGNITUDE OF THE MOMENTUM
63 P=DSQRT(PX**2+PY**2+PZ**2)
64 C THE COSINE OF THE ANGLE BETWEEN P AND R (FROM ATOM A TO B)
65 X=(-SIN(ALPHA)*PX+PZ*COS(ALPHA))/P
66 C DOT PRODUCT OF P AND R
67 PZR=P*RAD*X
68 C TEST THE TYPE OF MOLECULAR ORBITAL BEING DONE
69 IF (NTYPE.EQ. 2) GO TO 88
70 C THE CONTRIBUTION OF ATOM A TO REAL(CHI)
71 IF (N1S.EQ.0) GO TO 2
72 DO 1 I=1,N1S
73 1 RR=RR+C1S(I)*R1S(P,G1S(I))
74 2 IF (N2S.EQ.0) GO TO 4
75 DO 3 I=1,N2S
76 3 RR=RR+C2S(I)*R2S(P,G2S(I))
77 4 IF (N3S.EQ.0) GO TO 6
78 DO 5 I=1,N3S
79 5 RR=RR+C3S(I)*R3S(P,G3S(I))
80 6 IF (N4S.EQ.0) GO TO 8
81 DO 7 I=1,N4S
82 7 RR=RR+C4S(I)*R4S(P,G4S(I))
83 8 RR=PR*Y00(X)
84 88 IF (N3D.EQ.0) GO TO 10
85 A=0.000
86 DO 9 I=1,N3D
87 9 A=A+C3D(I)*R3D(P,G3D(I))
88 IF (NTYPE.EQ.1) RR=RR+A*Y20(X)
89 IF (NTYPE.EQ.2) RR=RR+A*Y21(X)
90 C CONTRIBUTION OF ATOM A TO IMAGINARY(CHI)
91 10 IF (N2P.EQ.0) GO TO 12
92 DO 11 I=1,N2P
93 11 RI=RI+C2P(I)*R2P(P,G2P(I))
94 12 IF (N3P.EQ.0) GO TO 14
95 DO 13 I=1,N3P
96 13 RI=RI+C3P(I)*R3P(P,G3P(I))
97 14 IF (N4P.EQ.0) GO TO 161
98 DO 15 I=1,N4P
99 15 RI=RI+C4P(I)*R4P(P,G4P(I))
100 161 IF (NTYPE.EQ.1) RI=RI *Y10(X)
101 IF (NTYPE.EQ.2) RI=RI *Y11(X)
102 IF (N4F.EQ.0) GO TO 16
103 A=0.000
104 DO 162 I=1,N4F
105 162 A=A+C4F(I)*R4F(P,G4F(I))
106 IF (NTYPE.EQ.1) RI=RI+A*Y30(X)
107 IF (NTYPE.EQ.2) RI=RI+A*Y31(X)
108 C NOW SUM THE CONTRIBUTION OF ATOM B
109 C RX WILL BE THE REAL PART, I.E., S AND D TYPES.
110 C RY WILL BE P AND F TYPES.
111 16 RX=C.000
112 RY=C.000
113 IF (NTYPE.EQ.2) GO TO 241
114 IF (M1S.EQ.0) GO TO 18
115 DO 17 I=1,M1S

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116      17      RX=RX+D1S(I)*P1S(P,H1S(I))
117      18      IF (M2S.EQ.0) GO TO 20
118      DO 19 I=1,M2S
119      19      RX=RX+D2S(I)*R2S(P,H2S(I))
120      20      IF (M3S.EQ.0) GO TO 22
121      DO 21 I=1,M3S
122      21      RX=RX+D3S(I)*R3S(P,H3S(I))
123      22      IF (M4S.EQ.0) GO TO 24
124      DO 23 I=1,M4S
125      23      RX=RX+D4S(I)*P4S(P,H4S(I))
126      24      RX=RX*YD0(X)
127      241     IF (M3D.EQ.0) GO TO 26
128      A=0.0D0
129      DO 25 I=1,M3D
130      25      A=A+D3D(I)*R3D(P,H3D(I))
131      IF (NTYPE.EQ.1) RX=RX+A*Y20(X)
132      IF (NTYPE.EQ.2) RX=RX+A*Y21(X)
133      26      IF (M2P.EQ.0) GO TO 28
134      DO 27 I=1,M2P
135      27      RY=RY+D2P(I)*R2P(P,H2P(I))
136      28      IF (M3P.EQ.0) GO TO 30
137      DO 29 I=1,M3P
138      29      RY=RY+D3P(I)*R3P(P,H3P(I))
139      30      IF (M4P.EQ.0) GO TO 32
140      DO 31 I=1,M4P
141      31      RY=RY+D4P(I)*R4P(P,H4P(I))
142      32      IF (NTYPE.EQ.1) RY=RY*Y10(X)
143      IF (NTYPE.EQ.2) RY=RY*Y11(X)
144      IF (M4F.EQ.0) GO TO 34
145      A=0.0D0
146      DO 33 I=1,M4F
147      33      A=A+D4F(I)*P4F(P,H4F(I))
148      IF (NTYPE.EQ.1) RY=RY+A*Y30(X)
149      IF (NTYPE.EQ.2) RY=RY+A*Y31(X)
150      C CONTRIBUION OF ATOM B TO REAL(CHI)
151      34      RR=RR+RX*DCOS(PZR)+RY*DSIN(PZR)
152      C CONTRIBUION TO IMAG(CHI)
153      RI=RI-RY*DSIN(PZR)+RX*DCOS(PZR)
154      C NOW CHISQ IS GIVEN BY
155      CHISQ=RR**2+RI**2
156      RETURN
157      END

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1      C *****
2      C THIS PROGRAM WILL CALCULATE THE TOTAL MOLECULAR COMPTON
3      C PROFILES AND THE CRYSTALLINE PROFILES FOR AN FCC CRYSTAL.
4      C THE ANISOTROPIES ARE THEN CALCULATED. DATA IS READ FROM
5      C A PREVIOUS FILE CREATED BY THE MAIN PROGRAM.
6      C INC IS THE OCCUPATION NUMBER OF THE MO.
7      C *****
8          REAL INC
9          DIMENSION PZ(50),X00(50),X45(50),X55(50),X90(50)
10         DO 11 I=1,50
11             X00(I)=0
12             X45(I)=0
13             X55(I)=0
14             11 X90(I)=0
15             READ 100,NO
16         C NO IS THE NUMBER OF MO'S
17             DO 1 J=1,NO
18                 READ 100,NTYPE,INC
19         C NPZ IS THE NUMBER OF PZ'S USED IN THE CALCULATION.
20             READ 200,NPZ
21             100 FORMAT( )
22             200 FORMAT(/,I3)
23             IF (J.GE.NO) PRINT 400
24         C Y1 IS THE 0-90 ANISOTROPY.
25         C Y2 IS THE J(100) CP, Y3 IS THE J(110) CP, X55 IS J(111)
26         C Y4 TO Y6 ARE THE CRYSTALLINE ANISOTROPIES.
27         C Y0 IS THE AVERAGE COMPTON PROFILE.
28         C RESULTS ARE PRINTED FOR EACH MO
29             DO 2 I=1,NPZ
30                 READ 300,PZ(I),A,B,C,D
31                 X00(I)=X00(I)+INC*A
32                 X45(I)=X45(I)+INC*B
33                 X55(I)=X55(I)+INC*C
34                 X90(I)=X90(I)+INC*D
35                 IF(J.LT.NO)GO TO 2
36             5 Y1=X00(I)-X90(I)
37                 Y2=(2*X90(I)+X00(I))/3.
38                 Y3=(2*X45(I)+X90(I))/3.
39                 Y4=Y2-Y3
40                 Y5=Y2-X55(I)
41                 Y6=Y3-X55(I)
42                 Y0=(3*Y2+6*Y3+4*X55(I))/13.
43                 PRINT 500,PZ(I),Y2,Y3,X55(I),Y0,X00(I),X45(I),X90(I),
44                 * Y1,Y4,Y5,Y6,PZ(I)
45             2 CONTINUE
46             1 CONTINUE
47         400 FORMAT('1',//,2X,'PZ',7X,'100',7X,'110',7X,'111',7X,
48         * 'AVG',7X,'000',7X,'450',7X,'900',6X,'0-90',5X,'100-110',
49         * 3X,'100-111',3X,'110-111',2X,'PZ'/)
50             300 FORMAT(F5.2,4(2X,F8.4))
51             500 FORMAT(1X,F4.1,11(2X,F8.4),2X,F4.1)
52             STOP
53             END

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