

On the Vibrational Average of Diatomic Molecular Form Factors: A Study of the Convolution Approximation

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(Received 16 August 1978; accepted 4 January 1979)

Abstract

The zero-point vibrational average of molecular form factors for diatomic molecules is treated as an observable from X-ray diffraction measurements. This model allows exploration of the influence of a single internal vibration on $F_{\text{Bragg}}(\mathbf{S})$. It is found that when anharmonic terms in the atomic vibration are included, then deconvolution to the static form factor, $F(\mathbf{S}; R_e)$ is achieved. Neglect of the anharmonic terms gives rise to spurious sharp dipole features in the heavy-pseudoatom charge densities, but not to the H-pseudoatom charge density. Non-rigid terms in the pseudoatoms are virtually negligible except for H where the non-rigid effect is as large as 6% in the hydrogen quadrupole scattering factor. The diatomic molecules studied include $\text{N}_2(^1\Sigma_g^+)$, $\text{CO}(^1\Sigma^+)$, $\text{BF}(^1\Sigma^+)$ and $\text{FH}(^1\Sigma^+)$.

Introduction

The elastic X-ray scattering intensity for a molecule or crystal with P nuclei at some position \mathbf{Q} (a $3P$ -dimensional vector) and with a one-electron density function $\rho(\mathbf{r}; \mathbf{Q})$ is

$$I_{\text{el}}^{XR}(\mathbf{S}; \mathbf{Q}) = |F(\mathbf{S}; \mathbf{Q})|^2, \quad (1)$$

where

$$F(\mathbf{S}; \mathbf{Q}) = \int \rho(\mathbf{r}; \mathbf{Q}) \exp(i\mathbf{S} \cdot \mathbf{Q}) d^3\mathbf{r}, \quad (2)$$

and \mathbf{S} is parallel to the Bragg vector and of magnitude $4\pi \sin \theta/\lambda$. (The Thomson cross-section and polarization factor are incorporated into I_{el}^{XR} .) The fundamental relations (1) and (2) are valid for kinematic scattering and for an incident X-ray frequency far above absorption frequencies of the target (Waller & Hartree, 1929). They also apply to a time scale short for a nuclear vibration. For X-ray frequencies large compared with nuclear vibrations, the observed intensity is a canonical ensemble average over the states for \mathbf{Q} ,

$$I_{\text{av}}(\mathbf{S}) = \sum_n W_n \int \chi_n(\mathbf{Q}) I_{\text{el}}^{XR}(\mathbf{S}; \mathbf{Q}) \chi_n(\mathbf{Q}) d^3\mathbf{Q}, \quad (3)$$

where W_n is the Boltzmann weight factor for vibrational state n , with vibrational wavefunction $\chi_n(\mathbf{Q})$. In

general (3) contains inelastically scattered intensities due to vibrons in the molecule or to phonons in the lattice. In crystallography the contribution is often called thermal diffuse scattering. For most X-ray diffraction experiments ($\nu_0 \simeq 3 \times 10^{18} \text{ s}^{-1}$) these phonon-induced, inelastically scattered components cannot be measured by X-ray monochromators or other energy analyzers since, at the least, an energy or frequency resolution of 10^{-5} (more appropriately 10^{-7}) is required. Moreover, (3) cannot be simply related to a vibrational average of the electron charge-density function in the molecule or crystal.

Born (1942–1943) carried out a detailed analysis of (3) with harmonic oscillator functions for $\chi_n(\mathbf{Q})$ and rigid pseudoatoms (essentially atomic form factors) for an explicit representation of $F(\mathbf{S}; \mathbf{Q})$. In this model,

$$I_{\text{av}} = \sum_p \sum_{p'} \sum_{k=0}^{\infty} \mathcal{F}_p \{ |\mathbf{S}^\dagger \mathcal{S}_{pp'} \mathbf{S} / (m_p m_{p'})^{1/2} |^k / k! \} \mathcal{F}_p^*, \quad (4)$$

where

$$\mathcal{F}_p = f_p(\mathbf{S}; \mathbf{Q}^0) \exp(i\mathbf{S} \cdot \mathbf{Q}^0) \exp(-\frac{1}{2} \mathbf{S}^\dagger \mathcal{Z}_p \mathbf{S}) \quad (5)$$

and $\mathcal{S}_{pp'}$ is the Born (1942–1943) scattering matrix that couples atom p to atom p' . In (5) \mathcal{Z}_p is the tensor for the mean-square amplitudes of motion for atom p , $f_p(\mathbf{S}; \mathbf{Q}^0)$ is the generalized X-ray scattering factor for pseudoatom p and \mathbf{Q}^0 is the time-average position for atom p . Note that (5) is the usual term for an atom in a structure factor equation. Born then shows that in a crystal for which von Laue interference terms are dominant, the $k=0$ term in (4) is the major contributor to I_{av} when $\mathbf{S} = 2\pi\mathbf{H}$, and \mathbf{H} is the usual Bragg vector in terms of Miller indices. The $k=1$ term can also peak under the Bragg intensity (I_{av} for $k=0$), but is rather smaller for small values of $|\mathbf{S}|$. Each k term in (4) is often associated with k -phonon scattering. The Born model gives us a theoretical foundation for Debye's original structure-factor formulation (Debye, 1930). For crystal structure analysis, I_{av} in (4) truncated at $k=0$, is usually invoked and is often called the Bragg intensity,

$$I_{\text{Bragg}}(\mathbf{S}) = |F_{\text{Bragg}}(\mathbf{S})|^2, \quad (6)$$

where

$$F_{\text{Bragg}}(\mathbf{S}) = \sum_p \mathcal{F}_p \quad (7)$$

and \mathcal{F}_p is given by (5). It is not at all clear that (6) is adequate for charge-density analysis from real X-ray diffraction data.

Assuming harmonic motion and working backwards from (7) and (6) to the original formulation of vibrational averaging for an ensemble, we then discover that for (6) (Stewart, 1977),

$$I_{\text{Bragg}}(\mathbf{S}) = |\sum W_n \langle \chi_n(\mathbf{Q}) F(\mathbf{S}; \mathbf{Q}) \chi_n(\mathbf{Q}) \rangle|^2, \quad (8)$$

where $\chi_n(\mathbf{Q})$ are for $3P$ harmonic oscillators and $F(\mathbf{S}; \mathbf{Q})$ is based on rigid pseudoatoms. Equation (8) is a curious result which is hard to understand on physical grounds. But (8) does show that within the Born model, $I_{\text{Bragg}}(\mathbf{S})$ is related to the Boltzmann weighted vibrational average of the charge-density function in a simple way. We do not know if (8) is applicable to the general adiabatic case where F is given by (2) and $\chi_n(\mathbf{Q})$ are the correct phonon wavefunctions (always anharmonic) for a lattice.

For the case where the temperature goes to zero,

$$I_{\text{av}}(\mathbf{S}) = \langle \chi_0(\mathbf{Q}) I_{\text{el}}^{\text{XR}}(\mathbf{S}; \mathbf{Q}) \chi_0(\mathbf{Q}) \rangle. \quad (9)$$

By completeness of $\chi_n(\mathbf{Q})$,

$$I_{\text{av}}(\mathbf{S}) = \sum_n \langle \chi_0(\mathbf{Q}) F^*(\mathbf{S}; \mathbf{Q}) \chi_n(\mathbf{Q}) \rangle \times \langle \chi_n(\mathbf{Q}) F(\mathbf{S}; \mathbf{Q}) \chi_0(\mathbf{Q}) \rangle. \quad (10)$$

For $n = 0$,

$$I_{\text{Bragg}}(\mathbf{S}) = |\langle \chi_0 F \chi_0 \rangle|^2, \quad (11)$$

and for $n \neq 0$,

$$I_{\text{TDS}}(\mathbf{S}) = \sum_{n \neq 0} |\langle \chi_0 F \chi_n \rangle|^2. \quad (12)$$

For the low-temperature result, it seems to be clear that I_{Bragg} is just the square of the zero-point vibrational average of the molecular form factor or crystal structure factor. To the extent that (11) is an observable, there is some interest in a study of $I_{\text{Bragg}}(\mathbf{S}; T \rightarrow 0)$.

In the present paper we take a pedagogical approach. We imagine that (11) is indeed an observable and moreover that

$$F_{\text{Bragg}}(\mathbf{S}; T \rightarrow 0) = \langle \chi_0(\mathbf{Q}) F(\mathbf{S}; \mathbf{Q}) \chi_0(\mathbf{Q}) \rangle \quad (13)$$

can be determined (both phases and amplitude). We choose to isolate the problem to a single vibration, so that a model which fundamentally violates the uncertainty principle is invoked. A diatomic molecule is assumed to be oriented with one degree of vibrational freedom. The other two directions of vibrational motion are, thought-wise, constrained to a vanishingly small amplitude of motion. We use this as a specialized model for (13) and seek to understand the influence of the anharmonic character of this single vibration on $F(\mathbf{S}; R)$ and the non-rigidity of pseudoatoms in response to the vibration.

The pseudoatom model for diatomics

Generalized X-ray scattering factors for the pseudoatoms can be determined directly from the diatomic molecular form factor $F_{\text{mol}}(\mathbf{S}; R)$ at several values of R . These functions are small, finite multipole expansions about each nucleus. For a specified expansion length about each center, the radial functions can be uniquely determined from the best mean-square fit to $F_{\text{mol}}(\mathbf{S}; R)$ (Stewart, Bentley & Goodman, 1975). In previous work (Bentley & Stewart, 1975), it was found that a [2|2] expansion reproduced $I_{\text{el}}^{\text{XR}}(\mathbf{S}; R)$ with a relative error no larger than 4×10^{-5} and that these six radial functions afforded a relative root-mean-square fit to $F_{\text{mol}}(\mathbf{S}; R)$ of 0.2%. For the present study we will use a [2|2] expansion.

$$F_{\text{mol}}^c(\mathbf{S}; R) = \exp(-i\mathbf{S} \cdot \mathbf{R}/2) \sum_{j=0}^2 i^j P_j(\eta) f_{a,j}(S; R) + \exp(i\mathbf{S} \cdot \mathbf{R}/2) \sum_{k=0}^2 i^k P_k(\eta) f_{b,k}(S; R), \quad (14)$$

where η is the direction cosine between \mathbf{S} and \mathbf{R} . Note in (14) that the bond midpoint is chosen as the phasing origin for $F_{\text{mol}}(\mathbf{S}; R)$. The procedure is to calculate $F_{\text{mol}}(\mathbf{S}; R)$ at several R 's about R_e from relatively accurate $\rho_{\text{mol}}(\mathbf{r}; R)$. The $f_{a,j}(S; R)$ and $f_{b,k}(S; R)$ are then determined from

$$\varepsilon(S) = \int |F_{\text{mol}} - F_{\text{mol}}^c|^2 d\Omega_S, \quad (15)$$

by minimizing (15) for each S :

$$\partial \varepsilon / \partial f_{a,j} = 0, \quad j = 0, 1, 2$$

$$\text{and } \partial \varepsilon / \partial f_{b,k} = 0, \quad k = 0, 1, 2. \quad (16)$$

Once the $\{f_a(S; R)\}$ and $\{f_b(S; R)\}$ are known, the Taylor expansions of $\{f_a\}$ about R_e ,

$$f_{a,j}(S; R) = f_{a,j}(S; R_e) + \left(\frac{\partial f_{a,j}}{\partial R} \right)_{R_e} (R - R_e) + \frac{1}{2} \left(\frac{\partial^2 f_{a,j}}{\partial R^2} \right)_{R_e} (R - R_e)^2 + \dots \quad (17)$$

and a similar expansion for the $\{f_b\}$ can be evaluated. The $f_{a,j}(S; R_e)$ and $f_{b,k}(S; R_e)$ define the rigid pseudoatom and the deforming pseudoatoms are given by the partial derivative functions. In general we expect the derivative terms in (17) to be non-zero since the $\{f_a\}$ and $\{f_b\}$ satisfy a large number of static charge properties of $\rho_{\text{mol}}(\mathbf{r}; R)$ at each R . In practice we found that first and second derivative terms were sufficient to give $f_{a,j}(S; R)$ and $f_{b,k}(S; R)$ to four or five figure accuracy. Also, as might be expected, the $(\partial f_{a,0} / \partial R)_{R_e}$ and $(\partial^2 f_{a,0} / \partial R^2)_{R_e}$ at large S become relatively small. The $f_{a,0}$ and $f_{b,0}$ at large S are the Fourier-Bessel

components of the pseudoatom charge-density near their respective nuclei. These local features of the monopoles should deform least.

A plot of $f_{F,2}(S;R)$ for the [2|2] fluorine pseudoatom in BF is shown in Fig. 1. The quadrupole scattering-factor curves were chosen for $\Delta R = \pm 0.4$ bohr (1 bohr = 0.529177 Å) of R_e . The corresponding charge-density components of the pseudoatom, for the three values of R , are shown in Fig. 2. In this case,

$$\rho_{F,2}(\mathbf{r}_F; R) = (2\pi^2)^{-1} P_2(\cos \theta_F) \times \int_0^\infty f_{F,2}(S; R) j_2(Sr_F) S^2 dS. \quad (18)$$

Fig. 1 and the corresponding direct-space picture in Fig. 2 clearly show that pseudoatoms can deform in a dramatic way. The question to pursue is of what consequence is this to the modeling of F_{Bragg} given by (13)? Details on the computation of (18) and other Fourier transforms of $\{f_a(S;R)\}$ and $\{f_b(S;R)\}$ as well as actual tabulations of the generalized X-ray scattering factors will be published elsewhere (Epstein & Stewart, 1979).

The electronic and vibrational wavefunctions

The diatomic molecules studied in this work are $N_2(^1\Sigma_g^+)$, $CO(^1\Sigma^+)$, $BF(^1\Sigma^+)$ and $FH(^1\Sigma^+)$. In this series, the root-mean-square amplitude of vibration increases. The electronic wavefunctions are near Hartree-Fock quality and employ extensive basis sets

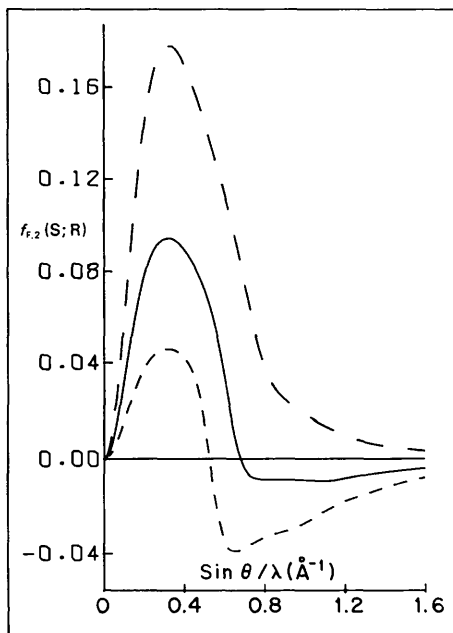


Fig. 1. [2|2] fluorine pseudoatom quadrupole scattering-factors from BF for different internuclear distances, R . Solid curve $R = 2.391$, short dash $R = 2.770$, long dash $R = 2.000$ a.u. (1 a.u. = 0.529177 Å).

of Slater-type functions. These wavefunctions at several R values are published in the literature: N_2 , Cade & Wahl (1974) and Cade, Sales & Wahl (1966); CO , Huo (1965); BF , McLean & Yoshimine (1976); FH , Cade & Huo (1967). The computation of molecular form factors was by procedures previously reported (Bentley & Stewart, 1973). The $\{f_a\}$ and $\{f_b\}$ at [2|2] expansion were determined by the methods of Stewart, Bentley & Goodman (1975).

A vibrational potential function, $U(R)$, was determined from the total energy of the diatomic electronic wavefunctions cited above. We chose to expand $U(R)$ to the cubic term only,

$$U(R) = \frac{1}{2} \left(\frac{d^2 U}{dR^2} \right)_{R_e} (R - R_e)^2 + \frac{1}{6} \left(\frac{d^3 U}{dR^3} \right)_{R_e} (R - R_e)^3. \quad (19)$$

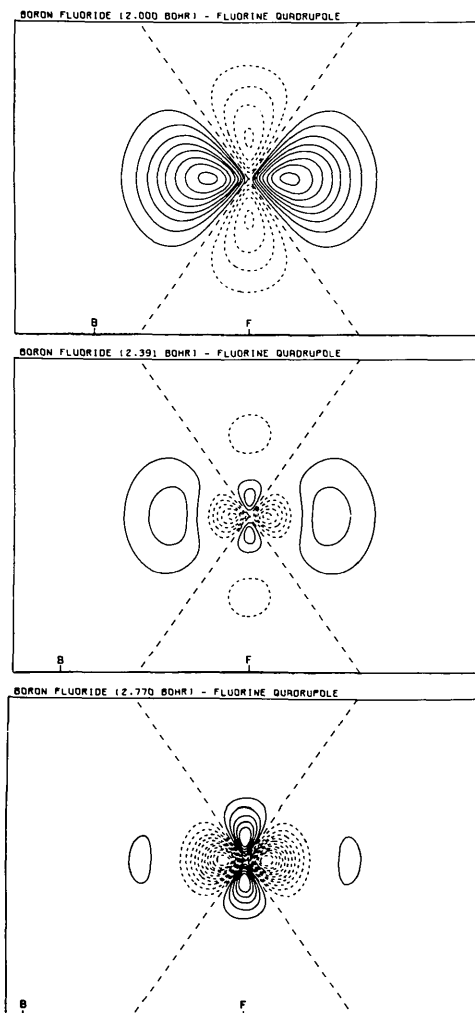


Fig. 2. The fluorine pseudoatom quadrupole electron-density functions from [2|2] fit to BF at $R = 2.000$, 2.391 and 2.770 a.u. respectively. Contours in units of $0.01 e/(a.u.)^3$. Solid curve positive, short dash negative [$1 e/(a.u.)^3 = 6.75 e/\text{Å}^3$].

By treating the cubic term as a perturbation, the ground state vibrational wavefunction, to first order,

$$\chi_0(R) = \varphi_0(R) + C_1 \varphi_1(R) + C_3 \varphi_3(R), \quad (20)$$

where the $\varphi_n(R)$ are harmonic oscillator wavefunctions,

$$\begin{aligned} \varphi_n(R) = & \left(\frac{\alpha}{\sqrt{\pi} 2^n n!} \right)^{1/2} R^{-1} H_n[\alpha(R - R_e)] \\ & \times \exp[-\alpha^2(R - R_e)^2/2]. \end{aligned} \quad (21)$$

In (21) $\alpha^2 = [2\langle X_{12}^2 \rangle]^{-1}$ and $\langle X_{12}^2 \rangle$ is the mean-square amplitude of vibration. $H_n(y)$ is the Hermite polynomial of order n . The functions in (21) are an exact solution for the harmonic potential [(19) sans cubic term] if $(\alpha R_e)^{-1} \ll 1$. The coefficients C_1 and C_3 for the approximate anharmonic wavefunction χ_0 in (20) are

$$\begin{aligned} C_1 = & - \left(\frac{d^3 U}{dR^3} \right)_{R_e} \mu \langle X_{12}^2 \rangle^{3/2} / \hbar, \\ C_3 = & \sqrt{(2/27)} C_1. \end{aligned} \quad (22)$$

In (22), μ is the reduced mass and \hbar is Planck's constant divided by 2π . The C_1 and C_3 parameters are dimensionless. The vibrational parameters for χ_0 in (20) are given in Table 1. Note that the mean-square amplitudes of vibration are very small compared with values often encountered in X-ray crystal structure analysis. The $\langle X_{12}^2 \rangle^{1/2}$ vary from 0.03 for N_2 to 0.06 Å for FH. Also note the approximate trend that the larger $\langle X_{12}^2 \rangle^{1/2}$, the larger the anharmonic coefficient C_1 .

Table 1. *Vibrational parameters*

	$\langle X_{12}^2 \rangle^{1/2}$ $\times 10^2$ (a.u.)*	$C_1 \times 10^2$	$C_3 \times 10^2$
N_2	5.6125	4.9393	1.3443
CO	6.0099	4.9185	1.3386
BF	7.5883	7.0979	1.9318
FH	11.864	11.533	3.1390

* 1 a.u. = 0.529177 Å = 0.529177 $\times 10^{-10}$ m.

The model for $F_{\text{Bragg}}(\mathbf{S})$

We consider the zero-point vibrational average of an 'oriented' diatomic molecule. This requires evaluation of (13). For the study here, the model for $F_{\text{Bragg}}(\mathbf{S})$ includes non-rigid pseudoatoms and an anharmonic potential for the vibration.

The diatomic molecular form-factor, $F(\mathbf{S}; R)$ is approximated with the [2|2] expansion, given by (14). The $\{f_a(\mathbf{S}; R)\}$ and $\{f_b(\mathbf{S}; R)\}$ are given by (17). Let \mathbf{U}_a be the displacement of nucleus a from equilibrium and \mathbf{U}_b the corresponding displacement vector for nucleus b .

The vibrational average (13) is then given explicitly,

$$\begin{aligned} F_{\text{Bragg}}(\mathbf{S}) = & \exp(-i\mathbf{S} \cdot \mathbf{R}_e/2) \sum_{j=0}^2 i^j P_j(\eta) \\ & \times \sum_{n=0}^2 \left(\frac{\partial^n f_{a,j}}{\partial R^n} \right)_{R_e} \langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_a) \rangle \\ & + \exp(i\mathbf{S} \cdot \mathbf{R}_e/2) \sum_{k=0}^2 i^k P_k(\eta) \\ & \times \sum_{n=0}^2 \left(\frac{\partial^n f_{b,k}}{\partial R^n} \right)_{R_e} \langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_b) \rangle. \end{aligned} \quad (23)$$

The notation, $\langle f(R) \rangle$, represents the average $\int \chi_0(R) f(R) \chi_0(R) R^2 dR$, with $\chi_0(R)$ given by (20). The algebraic forms of $\langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_a) \rangle$ and $\langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_b) \rangle$ are given in Table 2. In general these functions are complex. Terms of order C^2 are not included in Table 2, since these terms are of the same order as inclusion of a quartic term in (19). In powers of $\langle X_{12}^2 \rangle$, the first anharmonic term appears as $\langle X_{12}^2 \rangle^{1/2}$ and the first non-rigid term ($n = 1$) appears as $\langle X_{12}^2 \rangle$. For all the averages, the Debye-Waller-type function, $\exp(-S^2 \eta^2 \langle X_{12}^2 \rangle t_a)$, (or a corresponding function for center b) is a common factor.

Table 2. *Vibrational averages, $\langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_a) \rangle$ and $\langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_b) \rangle$ in terms of the Bragg vector and vibrational wavefunction parameters and atomic masses, m_a and m_b*

n	$\langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_a) \rangle$ or $\langle (\Delta R)^n \exp(i\mathbf{S} \cdot \mathbf{U}_b) \rangle$
0	$\exp[-S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2/2] [1 - i(2C_1 S \eta \langle X_{12}^2 \rangle^{1/2} t_a - (2/3)^{1/2} C_3 S^3 \eta^3 \langle X_{12}^2 \rangle^{3/2} t_a^3)]$
1	$\langle X_{12}^2 \rangle^{1/2} \exp[-S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2/2] [-iS \eta \langle X_{12}^2 \rangle^{1/2} t_a + 2C_1 (1 - S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2) - (2/3)^{1/2} C_3 S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2 \times (3 - S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2)]$
2	$\langle X_{12}^2 \rangle \exp[-S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2/2] (1 - S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2 - i\{2C_1 S \eta \langle X_{12}^2 \rangle^{1/2} t_a (3 - S^2 \eta^2 \langle X_{12}^2 \rangle t_a^2) + (2/3)^{1/2} C_3 [S \eta \langle X_{12}^2 \rangle^{1/2} t_a]^3 - 7(S \eta \langle X_{12}^2 \rangle^{1/2} t_a)^3 + 6S \eta \langle X_{12}^2 \rangle^{1/2} t_a\})$

$$t_a = m_b/(m_a + m_b); t_b = -m_a/(m_a + m_b); i = \sqrt{-1}$$

η is the direction cosine between \mathbf{S} and \mathbf{R} (the internuclear vector).

The deconvolution problem

We now pose the following problem in a study of the convolution approximation. It is assumed that (23) is an observable and we explore the question as to what extent $\{f_a(\mathbf{S}; R_e)\}$ and $\{f_b(\mathbf{S}; R_e)\}$ can be recovered

from (23) with a pseudoatom model. We define,

$$F_{\text{Bragg}}^{\text{Rigid}}(\mathbf{S}) = \exp(-i\mathbf{S} \cdot \mathbf{R}_e/2) \langle \exp(i\mathbf{S} \cdot \mathbf{U}_a) \rangle \\ \times \sum_{j=0}^2 i^j g_{a,j}(S) P_j(\eta) \\ + \exp(i\mathbf{S} \cdot \mathbf{R}_e/2) \langle \exp(i\mathbf{S} \cdot \mathbf{U}_b) \rangle \\ \times \sum_{k=0}^2 i^k g_{b,k}(S) P_k(\eta). \quad (24)$$

In (24) pseudoatom atom a , $\{g_a\}$, is assigned the vibrational parameters in $\langle \exp(i\mathbf{S} \cdot \mathbf{U}_a) \rangle$ given in Table 2 and corresponding parameters are assigned to $\{g_b\}$. In direct space, the first term is the convolution of the $\{g_a\}$ pseudoatom charge density onto the anharmonic nuclear distribution function, which is given by the Fourier transform of $\langle \exp i\mathbf{S} \cdot \mathbf{U}_a \rangle$. The second term in (24) is the corresponding convolution of the $\{g_b\}$ pseudoatom onto the nuclear distribution function for b . We form the mean-square function,

$$\varepsilon(S) = \int_{-1}^1 \int_0^{2\pi} |F_{\text{Bragg}}(\mathbf{S}) - F_{\text{Bragg}}^{\text{Rigid}}(\mathbf{S})|^2 d\eta d\phi_S, \quad (25)$$

and for each S minimize $\varepsilon(S)$ with respect to $g_{a,j}(S)$ and $g_{b,k}(S)$;

$$\partial \varepsilon(S) / \partial g_{a,j} = 0, \quad j = 0, 1, 2$$

$$\text{and } \partial \varepsilon(S) / \partial g_{b,k} = 0, \quad k = 0, 1, 2. \quad (26)$$

We may then compare $\{g_a(S)\}$ to $\{f_a(S; R_e)\}$ and $\{g_b(S)\}$ to $\{f_b(S; R_e)\}$. If the g 's are close to the f 's, then a successful deconvolution of $F_{\text{Bragg}}(\mathbf{S})$ to a static charge, $F(\mathbf{S}; R_e)$, has been accomplished.

The solution to (26) has been divided into two categories. In the first case, $C_1 = C_3 = 0$ in (24), so that only an harmonic motion is assumed for $F_{\text{Bragg}}^{\text{Rigid}}(\mathbf{S})$. In this case the g 's from a solution to (26) are denoted $g_{a,j}^H(S)$ and $g_{b,k}^H(S)$. The second set of solutions from (26) include the anharmonic terms in (24), and the 'atom' scattering-factors are simply denoted as $g_{a,j}(S)$ and $g_{b,k}(S)$.

Results

It is useful to compare the $\{g_p^H(S)\}$ and $\{g_p(S)\}$ with the $\{f_p(S; R_e)\}$ multipole by multipole (p is a or b). The monopole scattering-factors $g_{p,0}^H$ and $g_{p,0}$ from N_2 , CO and BF differ from $f_{p,0}(S; R_e)$ by less than two parts in one thousand. This is also the case for $g_{F,0}^H$ and $g_{F,0}$ in FH . For $g_{H,0}^H$, however, the maximum difference is 2% at $\sin \theta/\lambda = 0.04 \text{ \AA}^{-1}$ and for $g_{H,0}$, the maximum relative difference from $f_{H,0}(S; R_e)$ is 0.16% at 0.28 \AA^{-1} in $\sin \theta/\lambda$.

In strong contrast to the monopoles, the $g_{p,1}^H(S)$ for all the heavy pseudoatoms differ appreciably from $f_{p,1}(S; R_e)$. Plots of these scattering factors are dis-

played in Fig. 3 for N , C , O , B and both F pseudoatoms respectively. In all cases the $g_{p,1}^H(S)$ give a contracted dipole component of opposite planarity and larger magnitude than for the pseudoatom at R_e . The $g_{p,1}^H(S)$ from (26) contain components due to the coupling of monopole scattering-factors and the anharmonic terms in $F_{\text{Bragg}}(S)$ from (23). The dominant contribution to the dipole function for pseudoatom a projected from $F_{\text{Bragg}}(S)$ into $g_{a,1}^H(S)$ is

$$f_{a,1}(S; R_e) - 2t_a C_1 \langle X_{12}^2 \rangle^{1/2} S f_{a,0}(S; R_e).$$

A similar term occurs for the projection of $F_{\text{Bragg}}(S)$ into $g_{b,1}^H(S)$. The largest discrepancy between $g_{p,1}^H(S)$ and $f_{p,1}(S; R_e)$ occurs where $S f_{a,0}(S; R_e)$ is a maximum. Also shown in Fig. 3 are the $g_{p,1}(S)$ for the 'heavy' pseudoatoms. These form factors are negligibly different from $f_{p,1}(S; R_e)$. With inclusion of anharmonic terms, deconvolution of the vibrationally-averaged dipole functions to the static case is accom-

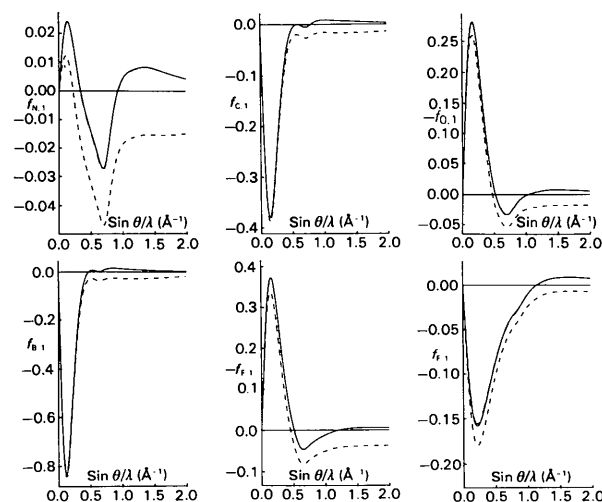


Fig. 3. [2|2] dipole scattering factors for N , C , O , B , F and F from N_2 , CO , BF and FH , respectively. Solid curve is $f_{p,1}(S; R_e)$, short dash is $g_{p,1}^H(S)$ and long dash is $g_{p,1}(S)$.

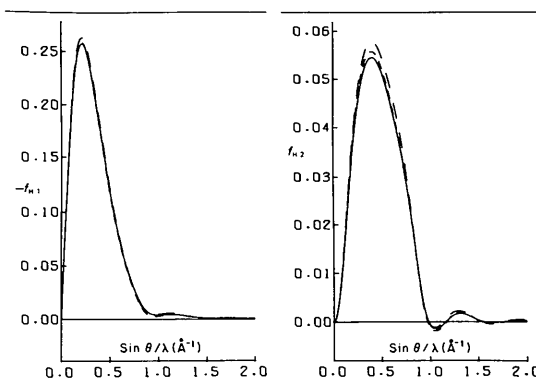


Fig. 4. [2|2] dipole and quadrupole scattering factors for H in HF as a function of $\sin \theta/\lambda$ (\AA^{-1}). Solid, short dash and long dash as described in Fig. 3.

plished. The dipole scattering-factors for the H pseudoatom in FH have rather different behavior to the heavier pseudoatoms. A plot of $-f_{H,1}(S;R_e)$, $-g_{H,1}^H(S)$ and $-g_{H,1}(S)$ is shown in Fig. 4. For this case, $g_{H,1}^H(S)$ does not differ appreciably from $f_{H,1}(S;R_e)$, but $g_{H,1}(S)$ does at $\sim 0.5 \text{ \AA}^{-1}$ in $\sin \theta/\lambda$. The apparent agreement between $f_{H,1}$ and $g_{H,1}^H$ is presumably due to the cancellation of the anharmonic and non-rigid effects, both of which are neglected in the rigid harmonic model. Also note that the $g_{H,1}^H$ does not have an artificial sharp dipole as do the other pseudoatoms.

The quadrupole scattering factors $g_{p,2}^H(S)$ for the heavy pseudoatoms are in much closer agreement with $f_{p,2}(S;R_e)$ than was found for the comparison of dipole scattering factors. The lighter atom typically has $g_{p,2}^H(S) > f_{p,2}(S;R_e)$ at the maximum difference, while for the heavier atom $g_{p,2}^H(S) < f_{p,2}(S;R_e)$. For $g_{N,2}^H(S)$ from N_2 , there is negligible difference from $f_{N,2}(S;R_e)$. For all the heavy pseudoatoms, $g_{p,2}(S)$ are essentially the same as $f_{p,2}(S;R_e)$ so that successful deconvolution is accomplished. The hydrogen pseudoatom quadrupole scattering factors from FH are also shown in Fig. 4. The $g_{H,2}^H(S)$ are closer to $f_{H,2}(S;R_e)$ than $g_{H,2}(S)$. As for the dipole case, the anharmonic and non-rigid effects partly cancel. The maximum difference of $f_{H,2}(S;R_e)$ from the anharmonic, rigid model is 6% while that for the harmonic, rigid model is 3% at 0.3 \AA^{-1} in $\sin \theta/\lambda$.

Conclusion

For the specialized study given here, a rigid pseudoatom model can recover $F(S;R_e)$ from $F_{\text{Bragg}}(S)$ provided that anharmonic contributions are included in the model. Non-rigid effects are found for the H pseudoatom and were as large as 6% for the quadrupole scattering factor. In earlier work (Stewart, 1977) it was argued for the three-dimensional case that generalized X-ray scattering factors, which guarantee a large number of static charge properties, cannot in general be extracted from $F_{\text{Bragg}}(S)$ in the zero temperature limit. In the present study, the zero-point vibration has been restricted to one dimension so that the convolution approximation can be appraised. If larger amplitudes of motion, such as libration, for these diatomics do not lead to appreciable deformation of the pseudoatoms, then it appears deconvolution can be achieved provided a correct nuclear distribution function is used. The dramatic breakdown of rigid pseudoatoms, displayed in Figs. 1 and 2, is of little consequence since $\langle X_{12}^2 \rangle$ for the diatomics considered in this work is rather small. Extension of the methods used

here to a three-dimensional problem is straightforward, but will be tedious and difficult to execute.

An analysis of non-rigid pseudoatoms in solids has been reported by March & Wilkins (1978). In this work the authors consider $\langle F_H \rangle$ as an observable. In this case their $\langle F_H \rangle$ is equation (8) here and is not restricted to the zero-temperature limit. These workers conclude that non-rigid effects are very small, but they do not consider anharmonic contributions to the model.

Lastly, we point out that the convolution model in this work [equation (24)] should not be confused with the convolution approximation used by Coulson & Thomas (1971) in an analysis of the H_2 molecule. For the present study a pseudoatom is assumed to rigidly follow its associated nucleus. In the Coulson-Thomas study, the molecular charge-density at R_e , $\rho_{\text{mol}}(\mathbf{r};R_e)$, is convoluted onto the square of the vibrational wavefunction. Coulson & Thomas use an harmonic oscillator wavefunction, so that in their model, $F_{\text{Bragg}}(\mathbf{S}) = F_{\text{mol}}(\mathbf{S};R_e) \exp(-S^2 \eta^2 \langle X_{12}^2 \rangle / H)$. This is the same as equation (24) if anharmonic terms are neglected and if the diatomic molecule is homonuclear.

We are grateful to Professors Paul Cade and Richard Bader for communicating to us Hartree-Fock wavefunctions of FH at several R values near R_e . This research was supported by NSF Grant CHE-77-09649.

References

- BENTLEY, J. & STEWART, R. F. (1973). *J. Comput. Phys.* **11**, 127-145.
- BENTLEY, J. & STEWART, R. F. (1975). *J. Chem. Phys.* **63**, 3794-3803.
- BORN, M. (1942-1943). *Rep. Prog. Phys.* **9**, 294-333.
- CADE, P. E. & HUO, W. (1967). *J. Chem. Phys.* **47**, 614-648.
- CADE, P. E., SALES, K. D. & WAHL, A. C. (1966). *J. Chem. Phys.* **44**, 1973-2003.
- CADE, P. E. & WAHL, A. C. (1974). *At. Data Nucl. Data Tables*, **13**, 371.
- COULSON, C. A. & THOMAS, M. W. (1971). *Acta Cryst.* **B27**, 1354-1359.
- DEBYE, P. (1930). *Phys. Z.* **31**, 419-428.
- EPSTEIN, J. & STEWART, R. F. (1979). *J. Chem. Phys.* **70**. In the press.
- HUO, W. (1965). *J. Chem. Phys.* **43**, 624-647.
- MCLEAN, A. D. & YOSHIMINE, M. (1976). *I.B.M. J. Res. Dev.* **12**, Suppl. 20-26.
- MARCH, N. H. & WILKINS, S. W. (1978). *Acta Cryst.* **A34**, 19-26.
- STEWART, R. F. (1977). *Isr. J. Chem.* **16**, 137-143.
- STEWART, R. F., BENTLEY, J. & GOODMAN, B. (1975). *J. Chem. Phys.* **63**, 3786-3793.
- WALLER, I. & HARTREE, D. R. (1929). *Proc. R. Soc. London Ser. A*, **124**, 119-142.