

***Ab initio* calculations of the hydrogen bond**B. Barbiellini<sup>1</sup> and A. Shukla<sup>2,\*</sup><sup>1</sup>*Department of Physics, Northeastern University, Boston, Massachusetts 02115*<sup>2</sup>*European Synchrotron Radiation Facility, Boîte Postale 220, Grenoble, France*

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Recent x-ray Compton scattering experiments in ice have provided useful information about the quantum nature of the interaction between H<sub>2</sub>O monomers. The hydrogen bond is characterized by a certain amount of charge transfer which could be determined in a Compton experiment. We use *ab initio* simulations to investigate the hydrogen bond in H<sub>2</sub>O structures by calculating the Compton profile and related quantities in three different systems, namely, the water dimer, a cluster containing 12 water molecules, and the ice crystal. We show how to extract estimates of the charge transfer from the Compton profiles.

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**I. INTRODUCTION**

The hydrogen bond is one of the least well-understood components in the energy decomposition that is used to predict the folding of biological complexes such as proteins. Its importance stems from its directionality and modest bonding energies midway between strong covalent and weak van der Waals bonds. For this reason the intermolecular interaction is difficult to characterize. Recently, x-ray Compton scattering measurements in ice revealed subtle oscillations in the profile anisotropy, which can be interpreted as reflecting various quantum-mechanical aspects of the hydrogen bond.<sup>1-5</sup> In simple descriptions of the hydrogen bond,<sup>6-8</sup> the highest occupied molecular orbital (HOMO) of a proton acceptor monomer can be viewed as a lone pair *p* state of the oxygen, while the lowest unoccupied molecular orbital (LUMO) of the donor neighbor molecule is the antibonding OH orbital. Therefore, the problem can be reduced to an effective 2 × 2 eigenvalue calculation where the HOMO-LUMO mixing can, in principle, be measured by an angle  $\theta$ . In this effective model the amount of charge transferred can be defined as

$$\Delta Q = \int |\cos \theta \langle \mathbf{r} | 0 \rangle + \sin \theta \langle \mathbf{r} | 1 \rangle - \langle \mathbf{r} | 0 \rangle|^2 d^3 \mathbf{r}, \quad (1)$$

where  $\langle \mathbf{r} | 0 \rangle$  is the wave function of the lone pair and  $\langle \mathbf{r} | 1 \rangle$  is the wave function of the LUMO at the donor neighbor molecule. When the mixing is small, one obtains  $\Delta Q \approx \sin^2 \theta$ . Besides, in this limit,  $\sin \theta$  turns out to be approximately proportional to the energy gain due to the hydrogen bond.

Compton scattering gives us information on the (ground state) electronic momentum distribution of the system under study. Of particular interest is the width  $\Delta p$  of the momentum density over which the valence momentum density falls to zero around a cutoff momentum (Fermi momentum in a metal). Since the LUMO contains higher momentum components than the HOMO, the variation of the width  $\Delta p$  is clearly related to the mixing  $\theta$ . Moreover, Friedel and Peter<sup>9</sup> provided a useful discussion on the impact in momentum density of the mixing of occupied with virtual orbitals. Their arguments can be extended to the present case in order to estimate the charge-transfer mixing angle. We limit our discussion here to the more general concept of charge transfer

without invoking the term covalency.<sup>6</sup> As a matter of fact ionic compounds are also characterized by a charge transfer but they are certainly not described as covalent systems.

This paper is organized as follows. In Sec. II we present the computational method and recall the definitions of the quantities studied. Section III is devoted to estimate the charge transfer and describe its properties in position space. Finally, Sec IV summarizes our main conclusions.

**II. METHOD**

We start with the one-particle density matrix  $\hat{\rho}(\mathbf{r}, \mathbf{r}')$ , which is defined in terms of the normalized *N*-particle wave function  $\Psi$  as

$$\hat{\rho}(\mathbf{r}, \mathbf{r}') = N \int d\xi \Psi^*(\mathbf{r}, \xi) \Psi(\mathbf{r}', \xi), \quad (2)$$

where the integral extends over the coordinates of all other particles. If the many-body wave function is represented by a single determinant, which is true in the Hartree-Fock case, then the density matrix is idempotent ( $\hat{\rho} = \hat{\rho}^2$ ) and reduces to a summation over the occupied spin-dependent orbitals  $\psi_i$ , i.e.,

$$\hat{\rho}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^N \psi_i(\mathbf{r}) \psi_i^*(\mathbf{r}'). \quad (3)$$

The electron momentum density (EMD) is defined as the momentum transform of the density matrix,

$$\rho(\mathbf{p}) = \frac{1}{8\pi^3} \int \int d^3 \mathbf{r} d^3 \mathbf{r}' \hat{\rho}(\mathbf{r}, \mathbf{r}') \exp[-i\mathbf{p} \cdot (\mathbf{r} - \mathbf{r}')]. \quad (4)$$

Note that, in general, the EMD involves off-diagonal elements of the real-space density matrix. In connection with the Compton spectra, it should be noted that the Compton profile,  $J(p_z)$ , represents the double integral of the ground-state EMD  $\rho(\mathbf{p})$ :

$$J(p_z) = \int \int \rho(\mathbf{p}) dp_x dp_y, \quad (5)$$

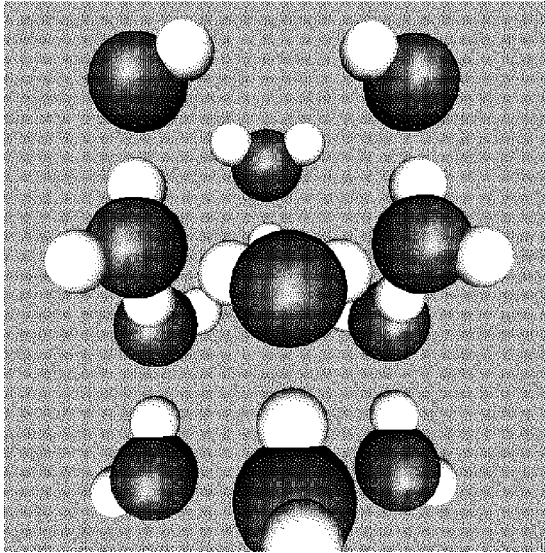


FIG. 1. Water cluster containing 12 water molecules.

where  $p_z$  lies along the scattering vector of the x rays.

The program used in the present work was CRYSTAL98,<sup>10</sup> which is especially appropriate for first-principles calculations of the density matrix  $\hat{\rho}(\mathbf{r}, \mathbf{r}')$  in extended (periodic) and molecular systems. For the ice crystal, we have used the experimental atomic distances. We have also considered the dimer and cluster containing 12 water molecules, which are shown in Fig. 1. The O-O distances and the orientations of the atoms in the cluster and in the dimer are equal to the corresponding ones in the crystal. The CRYSTAL98 program employs a linear combination of atomic orbitals for solving the Hartree-Fock equation. One can show that the wave function involved in the hydrogen bond are described reasonably well already at the level of the Hartree-Fock approximation.<sup>11,12</sup> The occupied orbitals used to determine the momentum density and the Compton profile are calculated using the restricted Hartree-Fock (RHF) scheme with the 6-31G\*\* basis set.<sup>12</sup>

### III. RESULTS

The density of state (DOS) of the ice crystal is shown in Fig. 2. The band gap is about 15 eV. In the occupied bands, one can notice two high peaks near  $-20$  eV and near  $-13$  eV. For comparison, in the dimer, the calculated RHF energies of the eight valence occupied states are  $-37$  eV,  $-36$  eV,  $-20$  eV,  $-19$  eV,  $-16$  eV,  $-15$  eV,  $-14$  eV, and  $-13$  eV. The electronic density of these dimer states has been visualized by Chaplin.<sup>13</sup> One can see that the densities of the orbitals corresponding to  $-19$  eV and to  $-15$  eV show overlap across the hydrogen bond. Interestingly, the two peaks of the crystal DOS correspond to dimer orbitals orthogonal to the hydrogen bond:  $-20$  eV corresponds to a state strongly localized on the acceptor molecule, while  $-13$  eV corresponds to a state localized on the donor water molecule. Clearly the dimer has some very important things to tell us about the nature of the hydrogen bond. The projected DOS shown in Fig. 3 reveals that the peak near

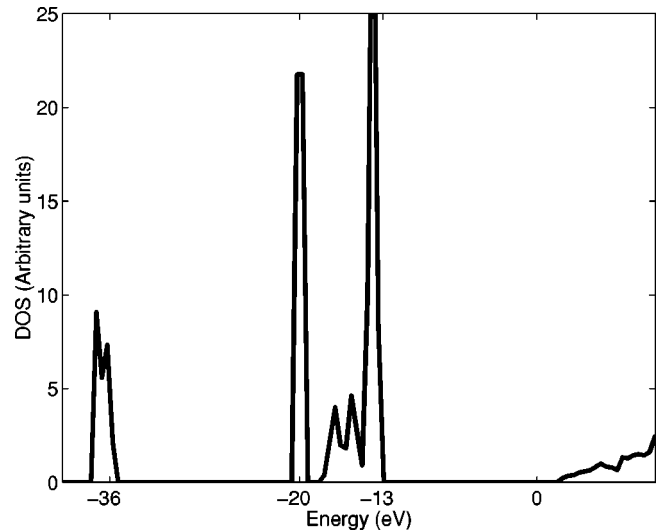


FIG. 2. DOS of the ice crystal according to the RHF calculation.

$-20$  eV is a combination of  $2p$  O and ( $1s$  H,  $2s$  H), while the peak near  $-13$  eV is almost a pure  $2p$  O. Moreover, one can notice that the highest occupied bands are mostly a combination of  $2p$  O and ( $1s$  H,  $2s$  H) states with a very small  $2s$  O contribution. This picture is therefore consistent with the charge-transfer theories<sup>7,8</sup> explaining the hydrogen bond by the mixing of the oxygen lone pair with an antibonding OH orbital centered on a neighbor molecule.

In order to extract molecular energies and other properties, it can be useful to build a density matrix as a superposition of density matrices of isolated molecules arranged in the same geometry as in the crystal or the cluster. The keyword MOLSPLIT (in the CRYSTAL98 input) performs an expansion of the lattice, in such a way that the molecules of the system are at an infinite distance from each other, to avoid intermolecular interactions. Our calculations indicate that the

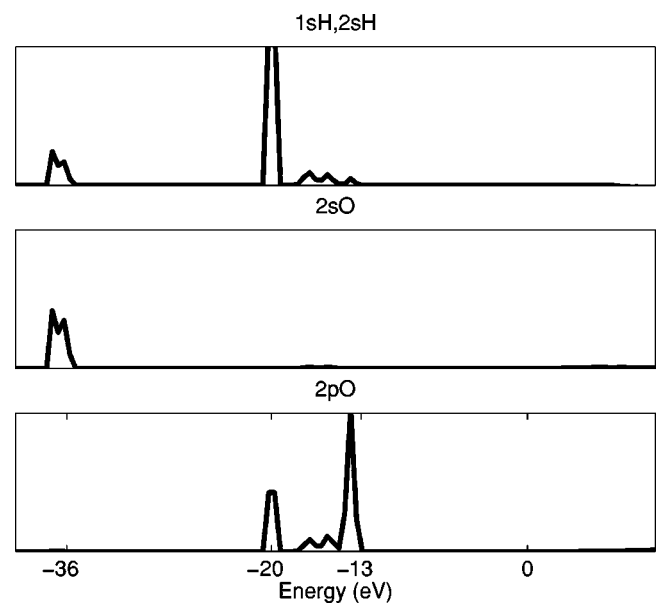


FIG. 3. Projected DOS per orbital of the ice crystal according to the RHF calculation.

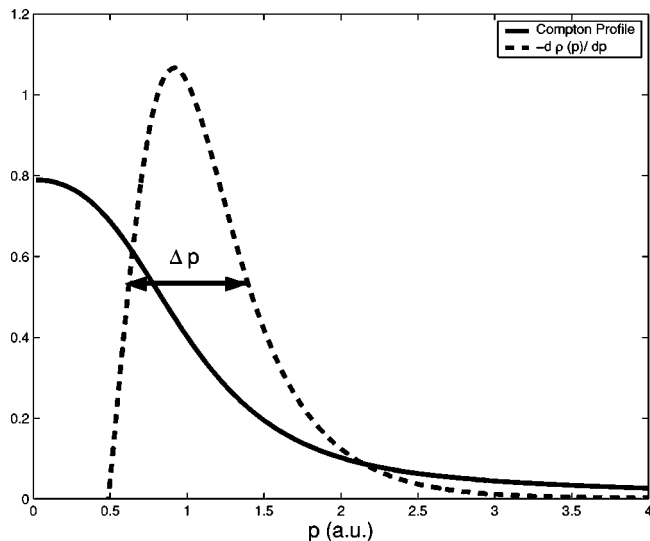


FIG. 4. Spherically averaged Compton profile  $J(p)$  of water (full line) together with the function  $-dn(p)/dp$  (dashed line) used to define the quantity  $\Delta p$ .

gain in energy per hydrogen bond in the crystal is  $-0.5$  eV. This energy gain is strengthened by a factor of 2 as one goes up in the cluster size.

Our aim in this work is to probe theoretically the effects of the hydrogen bond in water by evaluating the changes it provokes in the electronic momentum distribution, which can be probed using an experimentally accessible quantity, the Compton profile. For this, we use the spherical average of the momentum density  $n(p)$  which can be obtained from the isotropic or spherically averaged Compton profile  $J(p)$  by the formula

$$n(p) = \frac{1}{p} \frac{dJ(p)}{dp}. \quad (6)$$

The spherical averages  $J(p)$  and  $n(p)$  are thus used for the evaluation of a quantity  $\Delta p$ , defined as the full width at half maximum of the broad maximum exhibited by the function  $-dn(p)/dp$  (see Fig. 4). This maximum corresponds to the typical valence cutoff momentum (the Fermi momentum in the case of a metal). In the limit of a small mixing angle, formulas similar to those given by Friedel and Peter<sup>9</sup> indicate that  $\sin \theta$  is proportional to the variation of the momentum density smearing width. Moreover, by assuming a linear scaling between the momentum width and the energy separation of the effective  $2 \times 2$  eigenvalue problem, we obtain

$$\sin \theta \approx \frac{1}{\sqrt{2}} \frac{\Delta p - \Delta p_0}{\Delta p_0}, \quad (7)$$

where  $\Delta p_0$  corresponds to the single water molecule and  $\Delta p$  to the hydrogen bonded water structure being probed.

The radial derivative of  $-dn(p)/dp$  is shown in Fig. 5 for the water molecule, the dimer, the cluster containing 12 water molecules, and the ice crystal. The increase of  $\Delta p$  as a function of the cluster size is striking. The  $\sin \theta$  given by Eq. (7) is strengthened by a factor of 2 as one goes from the

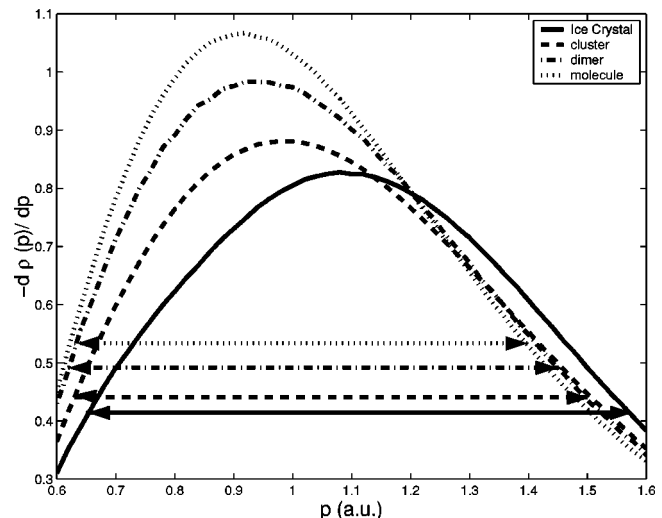


FIG. 5. Negative radial derivative of  $n(p)$  for the water molecule, the dimer, the cluster containing 12 water molecules, and the ice crystal.

dimer to the crystal. Thus, these estimates yield values consistent with the trends observed in the total-energy calculations. The amount of charge transferred is about 0.5% of an electron in the dimer, 1% in the cluster, and 2% in the crystal. Interestingly these values are in reasonable agreement with other estimates of the charge transfer given in previous quantum-mechanical calculations.<sup>7,8,14</sup> Finally, in Fig. 5 we also notice a shift of the maximum of the function  $-dn(p)/dp$  as a function of the cluster size, which can explain an observed increase of the kinetic energy.

In order to show how Compton scattering data can assist in the interpretation of the bonding properties in position space, one can define a function  $B(\mathbf{r})$ , which is the Fourier transform of the momentum density,<sup>15,16</sup>

$$B(\mathbf{r}) = \int \rho(\mathbf{p}) \exp(-i\mathbf{p} \cdot \mathbf{r}) d^3\mathbf{p}. \quad (8)$$

From the convolution theorem,  $B(\mathbf{r})$  is just the autocorrelation of the one-electron wave functions. Moreover,  $B(\mathbf{r})$  in a given direction can be calculated as the Fourier transform of the Compton profile in this direction. The orbital contribution of the  $1s$  core electron of oxygen vanishes beyond  $1.5 \text{ \AA}$  so that the  $B(\mathbf{r})$  is dominated by valence electrons. By analyzing  $B(\mathbf{r})$  in the direction  $z$  parallel to the hydrogen bond, we observe a negative local minima near  $2 \text{ \AA}$ , a positive local maximum near  $3 \text{ \AA}$  and finally a negative local minima at higher distances as shown in Fig. 6. The corresponding lines along  $x$  and  $y$ , also plotted in in Fig. 6, differ substantially from the  $z$  direction. Both  $x$  and  $y$  curves are quite similar and present only the local negative minima near  $2 \text{ \AA}$ , which is broader toward the large distances, and then their amplitudes go to zero at larger distances. The total autocorrelation function  $B(\mathbf{r})$  can be also interpreted in relation to the hydrogen bond with a comparison to isolated aligned molecules (obtained by MOLSPLIT). The isolated water molecules curves are shown in the bottom part of Fig. 6 along  $x$ ,  $y$ , and  $z$ . One can observe that none of these curves

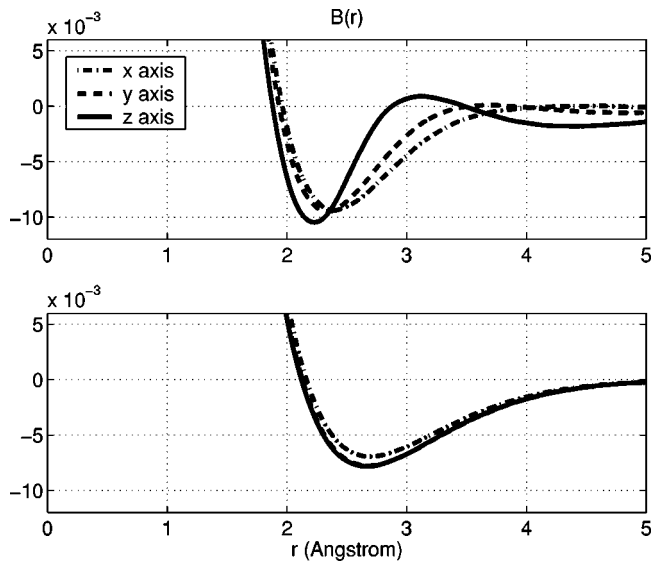


FIG. 6. Top: theoretical  $B(r)$  for the ice crystal along  $x$  (dashed-dot line),  $y$  (dashed line) and  $z$  (full line) directions obtained from the Compton profiles calculated by CRYSTAL98<sup>10</sup>. Bottom: corresponding lines for the isolated molecules. The lines are normalized so that  $B(0) = 1$ .

presents the oscillations that characterizes the  $z$  direction in the crystal. The autocorrelation function  $B(\mathbf{r})$  along the direction of the strongest hydrogen bond is shown in Fig. 7 for the crystal and the dimer. Both curves deviate strongly from the monomer curve. They also present some clear differences among them: the crystal possesses a deeper minimum and a somewhat lower maximum at 3 Å. However, beyond 4 Å the two curves cannot anymore be distinguished, indicating that the charge transfer occurs mostly within this distance range.

#### IV. CONCLUSION

In conclusion, this study confirms that the Compton profile is a useful tool for the investigation of the quantum nature of hydrogen bond in ice<sup>1</sup> and probably in other compounds such as urea,<sup>17</sup> RNA, and DNA.<sup>18</sup> Our results show a unique sensitivity of Compton scattering to the momentum width  $\Delta p$ . In this work an attempt has been made to give an estimate of the HOMO-LUMO mixing from Compton profiles. The present method can be also used for amorphous materials where Compton profiles anisotropies are not avail-

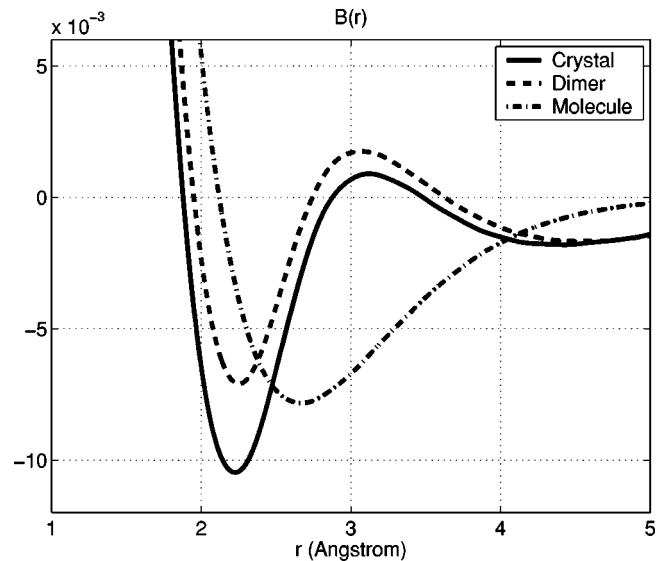


FIG. 7. Top: theoretical  $B(r)$  for the ice crystal (full line), the dimer (dashed line), and the water molecule (dashed-dot line) in the direction of the strongest hydrogen bond. The lines are normalized so that  $B(0) = 1$ .

able. Moreover, we have used the directional Compton profiles to study the bonding properties in the position space by using the autocorrelation functions. We have determined that the charge transfer occurs mostly within a range of about 4 Å. The present work also shows that x-ray inelastic-scattering experiments can shed light on the important role in short hydrogen bonds played by quantum-mechanical charge transfer between nearest molecules. These phenomena cannot be described by the standard effective classical potentials used, for instance in some water cluster simulations.<sup>19</sup>

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