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Hartree-Fock cluster investigation of ^{67}Zn nuclear quadrupole interaction in zinc oxide

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The nuclear quadrupole interaction of ^{67}Zn in the wurtzite structure for ZnO has been studied by the Hartree-Fock cluster procedure including the influence of lattice charges outside the chosen cluster. The nature of convergence of the electric-field gradient with the choice of basis set was studied and it was found important to have a flexible p basis set for oxygen. Additionally, the results using basis sets from neutral oxygen and O^{2-} in a Watson sphere were found to be of comparable magnitude. Our calculated value for the quadrupole coupling constant agrees very well with experiment.

I. INTRODUCTION

In this study we investigate the origin of ^{67}Zn nuclear quadrupole interaction (NQI) in perfect-lattice ZnO in the wurtzite phase. Zinc oxide is a relatively simple ionic solid in which experimental data for ^{67}Zn NQI are now available[1] through Mössbauer spectroscopy including temperature and pressure dependences. NQI provides a sensitive probe[2] of calculated electronic structures, especially the nonspherical distribution[3-5] of electron density at the nucleus. The understanding of the origin of ^{67}Zn NQI in perfect ZnO is therefore important for testing the Hartree-Fock cluster procedure for ionic solids and its application to more complex systems including impurity systems in ionic crystals and lattices distorted by external conditions such as hydrostatic and uniaxial pressures.

In the purely ionic model,[6] the atoms are replaced by point charges at the lattice sites equal to the formal charges of the ions involved. In some instances, the polarization effects of the lattice on the ions has been incorporated[7] in the model through inclusion of point multipole moments at the lattice sites obtained self-consistently. The limitations of the point-ion model are that it does not take account of the overlap of the electron distributions on neighboring ions or charge transfer covalency effects. Additionally it requires a choice of Sternheimer antishielding factors for the ions which can be rather sensitively influenced[8] by the penetration of one ion by the nuclear charges and electrons on neighboring ions. For these reasons, one can consider the results of point-ion model calculations[9] as semi-quantitative in nature. For a quantitative understanding of the NQI, the effects of overlap and covalency have to be explicitly included in a first-principles manner.[3,10] It is known that ZnO is partially covalent. For example, ZnO has a band gap[11] of 3.4 eV and is considered to be an oxide semiconductor.[12] Furthermore, the isomer shift in the ionic solid ZnF_2 has been observed[13] to be negative compared to ZnO which has been suggested to be a consequence of ZnF_2 having a more ionic character. The Hartree-Fock cluster procedure has proven[3,10,14] to be an especially useful technique for the calculation of localized phenomena such as hyperfine interactions in solids including NQI. In the present work we have carried out self-consistent Hartree-Fock calculations on a finite cluster of atoms with zinc at the center and the Madelung potential of the infinite solid included by embedding the cluster in an array of point charges.[3,10,15] Called the Hartree-Fock cluster procedure, this approach includes covalency effects in a first-principles manner. In this procedure there is no need to introduce any parameters for the Sternheimer antishielding effect for NQI in the solid since this effect is automatically included[3,10] in the calculation.

Section II gives the details of the crystal structure of ZnO and a brief description of the procedure used for electronic structure and NQI calculations. Section III contains the results and discussion, including comparison with experiment. Section IV presents a few concluding remarks.

II. PROCEDURE

Zinc oxide is a relatively simple ionic solid with the hexagonal wurtzite crystal structure and has lattice parameters[16] $a = 3.249858(6)$ Å and $c = 5.206619(2)$ Å at 298 K. The unit cell consists of two ZnO molecules with zinc atoms at (0,0,0) and (1/2,2/3,1/2) and oxygen atoms at $(0,0,u)$ and $(1/2,2/3,u+1/2)$ Wyckoff positions with $u = 0.3825(14)$. Each atom can be considered as being tetrahedrally coordinated by four atoms of the other kind. However, this tetrahedron is imperfect. The above lattice parameters yield a slight elongation in one direction resulting in a nonzero electric-field gradient (EFG). The asymmetry parameter is zero due to axial symmetry. The choice of crystal parameters that we have used for our work is very close to those from another recent x-ray diffraction measurement in the literature,[17] namely $a = 3.253(1)$ Å, $c = 5.213(1)$ Å, and $u = 0.3820(8)$. A much earlier measurement[18] in the literature had led to parameters which provided an oblate arrangement of oxygen atoms about the zinc, in contrast to the prolate character found in the more recent investigations.[16,17]

In the Hartree-Fock cluster procedure a finite number of atoms is chosen to represent the true infinite solid. The effects of the rest of the lattice outside the cluster are included by applying appropriate boundary conditions to the cluster. This is accomplished by embedding[3,15] the cluster in an array of point charges located at lattice positions of the true solid and having formal ionic charges $+2$ and -2 for Zn and O, respectively. Since only a finite number of point charges can be used in the calculation, the charges on the outermost shells are adjusted to exactly reproduce the Madelung potentials at the nuclei of all the atoms in the cluster and to maintain charge neutrality for the whole system of cluster plus point charges. For the study of ^{67}Zn NQI in ZnO, we have chosen the cluster $(ZnO_4)^{6-}$ with zinc at the origin. With this choice of cluster, interactions due to the nearest neighbors of zinc are included in a first-principles manner and the effect of the Madelung potential on the EFG is incorporated by combining the Hartree-Fock potential within the cluster with that due to the point charges at the lattice sites. With this treatment of the cluster and its environment, the infiniteness of the solid is incorporated into the calculation. For the EFG due to the charges outside of the cluster, Sternheimer antishielding effects[19] as mentioned in Sec. I are already incorporated through the influence of the potential due to these charges on the electron distribution within the cluster. The influence of Sternheimer antishielding effects due to the charges within the cluster is already included through the Hartree-Fock procedure which automatically incorporates the type of polarization effects associated with Sternheimer antishielding. One therefore does not have to introduce any approximate Sternheimer antishielding parameters inside the solid. As we will see from our results in Sec. III, and as has been found in earlier work, with this procedure, the major contribution to the EFG arises from the nuclear charges and electrons within the cluster.

The electronic structure associated with the system was calculated by the Hartree-Fock linear combinations of atomic orbitals–molecular-orbital (HF-LCAO-MO) procedure using the Gaussian-88 computer program. Gaussian-type functions (GTF) were used as the atomic basis sets. For zinc we have used a basis set composed of 14*s*, 9*p*, and 5*d* GTF's contracted to 8*s*, 4*p*, and 2*d* for neutral zinc atoms. This basis set was considered to be extensive enough for zinc in the present system from earlier studies[3] in ZnF_2. In the latter case 12*s* GTF's were employed, the two outermost GTF's being omitted to generate a Zn^{2+} basis set contracted to 6*s*, 4*p*, and 2*d* denoted as (62111111/5112/32) since zinc was considered to be ionic in that system. For ZnO, since one expects significant covalent bonding it was felt desirable to use the larger basis set involving all 14 GTF's of the *s* type. For oxygen which occurs as a diffuse negative ion in the crystal, we have attempted to study the dependence of the results on the choice of basis set by working with two alternatives. The first involved a neutral oxygen basis set consisting of 10*s* and 5*p* GTF's contracted to 3*s* and 2*p* referred to as (721/41). The second choice involved reoptimization of the neutral oxygen basis set for an O^{2-} ion inside a Watson sphere[20] of charge $+2$ (referred to as O_W^{2-} basis set) to simulate the solid-state environment.[3] The flexibilities of the O^0 and the O_W^{2-} basis sets were further tested by uncontracting the GTF's in different ways and by adding polarization functions involving *d* orbitals.

The calculated molecular orbital electronic wave functions for the cluster were utilized as usual to obtain the EFG at the zinc site, the asymmetry parameter being zero because of axial symmetry.

III. RESULTS AND DISCUSSION

With the HF cluster procedure we have investigated the convergence of the total energy and EFG with respect to the sizes and natures of the oxygen basis sets. This is accomplished by uncontracting the GTF's and adding polarization functions to the basis sets. We shall use these results to test different convergences with O^0 and O_W^{2-}, between O^0 and O_W^{2-} and with respect to polarization effects. For zinc, as mentioned in the preceding section we have made use of two extensive basis sets, one based on neutral zinc atom and the other based on Zn^{2+}. The results with the two basis sets are compared as a test of convergence with respect to the choice of basis set. Our results are also compared with experiment.

Table I gives the results of our HF calculations for total energy and EFG as the $O^0(3s,2p)$ or $O_W^{2-}(3s,2p)$ basis sets are increased in variational flexibility by uncontracting the GTF's or adding polarization functions. The first column gives the basis set along with the number of atomic orbitals and GTF's used in its construction. The second column gives the total energy from the HF cluster procedure. Finally, the third column gives the results for EFG of the $(ZnO_4)^{6-}$ cluster, the external point charges and the total EFG. As has been found in other systems from earlier work, the external contribution is very small compared to that from within the cluster.

It is evident from Table I that as the GTF's are uncontracted within either the O^0 or O_W^{2-} basis sets, the flexibility of the variational procedure increases and as expected the total energy continues to improve. As regards the EFG, the first two lines indicate that there is virtually no change on expanding the size of the *s*-basis set. Significant change in EFG occurs only when the *p* basis is uncontracted, especially from 2*p* to 3*p*. This result follows from the fact that *p* is the most directed oxygen orbital and so changes the bonding with Zn most significantly. The fact that the EFG for (3*s*,3*p*) is almost identical with (3*s*,5*p*) shows that convergence with respect to the size of the *p*-basis set has already been obtained at the 3*p* level. Comparing O^0 and O_W^{2-} shows that the energy favors O_W^{2-} for both the (3*s*,2*p*) and (3*s*,5*p*) basis sets. One could thus choose the O_W^{2-} EFG as we do for comparing with experiment but it is reassuring that O_W^{2-} and O^0 EFG are not too different. We use the small difference between the two results to decide on our confidence limit. The addition of a *d*-polarization function to form $O^0(3s,2p,1d)$ from $O^0(3s,2p)$ is seen from Table I to be not too significant for either the energy or

TABLE I. Results for EFG for ^{67}Zn for different choices of oxygen basis functions.

Choice of basis set	Energy (Hartrees)	q_{cluster}	q_{ext}	$q_{\text{total}}(a_0^{-3})$
$O^0(3s,2p)$:(721/41)	−2161.5502	0.071	−0.003	0.068
$O^0(4s,2p)$:(7111/41)	−2161.5529	0.071	−0.003	0.068
$O^0(3s,3p)$:(721/311)	−2161.8560	0.078	−0.003	0.075
$O^0(3s,5p)$:(721/11111)	−2161.8813	0.078	−0.003	0.075
$O^0(3s,2p,1d)$:(721/41/1)	−2161.5534	0.071	−0.003	0.068
$O_W^{2-}(3s,2p)$:(721/41)	−2162.0309	0.071	−0.003	0.068
$O_W^{2-}(3s,5p)$:(721/11111)	−2162.2178	0.074	−0.003	0.071

EFG. This is probably because the $3d$ is much too excited a state and one therefore expects very little mixing with the lower energy states.

Using the choice of $O_W^{2-}(3s,5p)$ basis set, which gives the lowest total energy, for comparison with experiment, we obtain the nuclear quadrupole coupling constant of $e^2qQ/h=2.50$ MHz, where the literature value[21] of $Q=0.150$ barns has been used for ^{67}Zn. Alternatively, taking the average of the total EFG for $O_W^{2-}(3s,5p)$ and $O^0(3s,5p)$ from Table I as the value for comparison with experiment and one-half their difference as the uncertainty, we obtain $e^2qQ/h=2.57(7)$ MHz. This is in very good agreement with the experimental value of $e^2qQ/h=2.401(4)$ MHz from Mössbauer measurements.[13]

IV. CONCLUSION

In conclusion, a comparison of the theoretical and experimental values of the EFG at ^{67}Zn in ZnO shows that a pretty realistic distribution of electron density has been obtained by the HF cluster procedure. The HF cluster procedure has included the Sternheimer effect and covalency in a first-principles manner. There is little difference in the calculated EFG's when one uses neutral or ionic oxygen basis sets.

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