The *ab initio* model potential representation of the crystalline environment. Theoretical study of the local distortion on NaCl:Cu$^+$

Zoila Barandiarán and Luis Seijo

Department of Chemistry, The University of Alberta, Edmonton, Alberta T6G 2G2, Canada and Departamento de Química, C-14, Universidad Autónoma de Madrid, 28049 Madrid, Spain

In this paper we formulate a model potential approach to take into account the crystalline environment within the Hartree–Fock–Roothaan formalism. The formulation is based on the assumption that the theory of separability of many-electron systems may be applicable to the group of electrons within a reference cluster and the groups of electrons on a set of external lattice sites which, in turn, can be represented according to the *ab initio* model potential method. The characteristics of the model potentials permit to analyze the contributions to the cluster energies and wave functions of different environmental effects, such as point-charge and charge-density Coulomb interactions and quantum interactions (exchange and orthogonality). The formalism is applied to the SCF calculation on the ground state of the octahedaral CuCl$_6^{5-}$ cluster (all-electron calculation) embedded in a NaCl lattice which is represented by 118 model-potential ions and 604 point-charge ions. The calculation reveals that (i) the quantum interactions between the CuCl$_6^{5-}$ cluster and the rest of the lattice play an important role in determining the Cu–Cl distance and (ii) a considerable local distortion around the Cu$^+$ impurity is predicted in which the Cl$^-$ ions move towards the Cu$^+$ impurity about 0.1 Å. These results are in qualitative agreement with recent EXAFS studies; however, the predicted distortion is smaller than the one suggested by the EXAFS measurements.

I. INTRODUCTION

It is well established from decades of chemical/physical experience that certain properties of (large) many-electron systems depend essentially on "relevant" portions of them. Examples of this can be found in molecules and solids: Many chemical properties of molecules are determined by the structure of valence electrons. Similarly, some properties of solids are believed to depend mainly on the electronic structure of small portions consisting of relatively few atoms or ions. The widespread use of terms like "core" and "valence" for molecules and "cluster," "neighbors," and "environment" for solids, as well as the amount of information ascribed to them, indicate the acceptance and vigor of the ideas mentioned above.

The old concepts attached to this experience, i.e., the separability of a many electron system into subsystems and localization, have considerably influenced the development of quantum mechanical methods suitable to study many electron systems such as large molecules and solids.[1-4]

An early precursor to more elaborate and exact methods oriented to the study of local properties of solids is the *cluster approximation* as applied to solid KNiF$_3$ by Sugano and Shulman[5]: Quantum mechanical methods usually developed for molecules are applied to the cluster while its environment is either neglected or classically treated as a set of point charges that create an electrostatic potential in which the cluster is immersed. Along the line of classical treatment of the environment, the external lattice potential is often evaluated through the Ewald method.[6] It is then included in the cluster Hamiltonian through an analytical representation[7] or through a discrete number of suitably located point charges that create equivalent electrostatic effects on the

cluster.[8] Alternatively, the infinite sum is truncated and a set of (fractional) point charges occupying experimentally determined ionic sites is included in the cluster calculation.[9,10] At this level of approximation, the parametrization of the ionic charges and/or of some interionic distances of the external lattice has proven to be necessary in some cases and has been interpreted as due to covalent effects.[11]

Kunz and Klein[12] have analyzed the use of the unrestricted Hartree–Fock (UHF) model for solid state cluster simulations. They avoid the solution of the UHF equations for the entire solid by considering some approximate forms of the local-orbital formalism of Adams and Gilbert.[1-3] In this way they have justified the model of a cluster embedded in a Madelung potential field for ionic and covalent crystals.[12]

More accurate representations of the crystalline environment are possible. On this line, the trend observed in *ab initio* cluster calculations points towards the use of higher quality (and more expensive) cluster wave functions.[10,13] This trend justifies the attempts to improve the lattice potentials so that (1) the number of constituents of the selected cluster can be kept to a minimum, and (2) a high quality, balanced representation of the cluster itself and of the cluster–lattice interaction is used. Either pseudo- or model potentials have been used for this purpose. Bonifacic–Huzinaga-type local model potentials[14] have been used by Katsuki and Taketa[15] in Hartree–Fock–Slater calculations in an attempt to annul the fictitious-surface effects which are brought into a finite-size-cluster model. Also, complete-cation pseudopotentials have been used in restricted Hartree–Fock calculations on ionic crystals by Winter, Pitzer, and Temple,[16,17] and in unrestricted Hartree–Fock calculations

by Vail and Pandey.[18] A problem remains on these calculations associated to the difficulty in obtaining complete-ion potentials, which has been partially overcome either using a local X_α approximation for the complete-ion exchange operator,[15] or using only complete-cation potentials and representing the complete anions by point charges.[16-18]

In this work, we formulate and apply the *ab initio* model potential approach to the crystalline environment effects within the Hartree–Fock formalism. The formulation, which is an extension of the *ab initio* model potential approach to the molecular core electron effects,[19] is based on the assumption that the theory of separability of many-electron systems formulated by Huzinaga *et al.*[4] may be applicable to the group of electrons within a reference cluster and the groups of electrons on a set of external lattice sites. If the many electron wave functions on the external lattice sites can be considered frozen, the theory[4] offers a means to calculate the total energy of the cluster taking into account all the interactions with the frozen environment. A final approximation is then introduced in order to make the calculations feasible: The *ab initio* model potential formalism presented in Ref. 19 is used to represent the effects of the frozen environment. This method has proven to be very close to its frozen orbital limit and to all-electron calculations,[19] and has the advantage over previous model potential formulations of leading to an accurate representation of the nonlocal exchange and orthogonality interactions. Within this formalism, the complete-ion potentials are obtained in a simple way, either for cations or anions. In addition, the method provides the means to carry out an analysis of all the cluster–lattice interactions contributing to the cluster electronic energy and wave function, namely, (i) point-charge electrostatic interactions, (ii) charge density electrostatic interactions, (iii) quantum exchange interactions, and (iv) quantum orthogonality interactions, thus allowing a more detailed and meaningful interpretation of the environmental effects. The details of the method are presented in Sec. II of this paper.

In Sec. III we present the results of a theoretical study of the local distortion around the Cu^+ impurity in NaCl:Cu^+. Although there exists some experimental evidence that the Cu^+ impurity ions occupy on site positions in the NaCl crystal substituting Na^+ ions,[20] the nature of the local geometry around the Cu^+ ions is not clear. Recent EXAFS studies[21] suggest the existence of a large lattice distortion around Cu^+, in which some of the Cl^- ions are closer to the Cu^+ than to the lattice Na^+ ions. These results contrast with those of previous X_α theoretical calculations[22] and recent *ab initio* RHF calculations[17] including complete-ion pseudopotentials for the lattice Na^+ ions and an accurate representation of the point-charge lattice Coulomb potential, which predict none or very small distortion. Here, we perform all-electron *ab initio* RHF calculations on octahedral $CuCl_6^{5-}$, taking into account the NaCl lattice effects through the *ab initio* model potential approach: including up to 118 Na^+ and Cl^- complete-ion model potentials, and 604 point-charge ions. A shortening of the Cu–Cl distance by 0.1 Å with respect to that of NaCl bulk is obtained, which is shown to be due to cluster–lattice quantum interactions (exchange

and orthogonality). The reliability of the results is tested by using a (linear NaCl):Cu^+ model in which the closest lattice ions can be treated at the all-electron level. The values obtained for the Cu–Cl equilibrium distance (2.681 Å) and the totally symmetric vibrational frequency (213 cm^{-1}) are expected to be closer than 0.05 Å and 36 cm^{-1}, respectively, to an all-electron *ab initio* RHF calculation including the nearest neighbors to $CuCl_6^{5-}$ in the cluster wave function.

II. METHOD

The formulation necessary to calculate the total energy of a cluster taking into account its interactions with the frozen crystalline environment within the lattice model potential approximation readily follows from that presented by Bonifacic and Huzinaga[14] for molecular systems having separable core and valence groups of electrons. We present here a summary in order to clarify the meaning of the terms and to facilitate the interpretation of the results.

We start by adopting the following approximate wave function to describe the crystalline system:

$$\Psi_{crys} \simeq MA_p [\Phi_{clus}\Phi_e\Phi_f\cdots\Phi_s], \tag{1}$$

where, for simplicity, Φ_{clus} is a closed-shell wave function representing the chosen N_c-electron cluster,

$$\Phi_{clus} = \sqrt{(1/N_c!)}\det[\psi_1^{clus}(1)\alpha(1)\psi_1^{clus}(2)$$
$$\times\beta(2)\cdots\psi_{N_c/2}^{clus}(N_c-1)\alpha(N_c-1)$$
$$\times\psi_{N_c/2}^{clus}(N_c)\beta(N_c)]. \tag{2}$$

(In general, Φ_{clus} could be either an open-shell SCF wave function or any multiconfigurational representation.)

$\Phi_e,\Phi_f,...,\Phi_s$ are closed-shell atomic wave functions representing the ions $e,f,...,s$ located on lattice sites outside the cluster

$$\Phi_e = (1/N_e!)\det[\phi_1^e(1)\alpha(1)\phi_1^e(2)\beta(2)\cdots\phi_{N_e/2}^e$$
$$\times(N_e-1)\alpha(N_e-1)\psi_{N_e/2}^e(N_e)\beta(N_e)] \tag{3}$$

and M and A_p are a normalization factor and the intergroup antisymmetrizer, respectively.

If the following orthornormal conditions are fulfilled:

$$\langle\phi_i^e|\phi_j^f\rangle = \delta_{ij}\delta_{ef}, \quad \langle\psi_i^{clus}|\psi_j^{clus}\rangle = \delta_{ij}, \tag{4}$$
$$\langle\psi_i^{clus}|\phi_j^e\rangle = 0,$$

the total energy of the system may be written as

$$E = \langle\Phi_{clus}|H_{clus}+H_{env}|\Phi_{clus}\rangle$$
$$+ \sum_e^{env}\langle\Phi_e|-\sum_i^{N_e}\sum_c^{clus}Z_c/r_{ci}|\Phi_e\rangle + \sum_c^{clus}\sum_e^{env}Z_cZ_e/r_{ce}$$
$$+ \sum_e^{env}E_e + \sum_{e>f}^{env}E_{e,f}, \tag{5}$$

where H_{clus} is the usual *in vacuo* nonrelativistic Hamiltonian and

$$H_{env} = \sum_i^{N_c}\sum_e^{env}\left\{-Z_e/r_{ei} + \sum_{k\in e}^{Ne/2}[2J_k(i)-K_k(i)]\right\}. \tag{6}$$

In Eq. (5), the first term collects the intracluster energy and the interaction energy between the environment and the

cluster electrons. The second and third terms represent the interaction energy between the cluster nuclei and the environment electrons and nuclei, respectively. Finally, the two last terms represent the environment energy and are constant contributions if the geometry and electronic densities of the environment are frozen.

The optimum Φ_{clus}, corresponding to the minimization of the total energy in Eq. (5) with respect *only* to the set $\{\psi_i^{\text{clus}}\}$ (note that the sets $\{\phi_i^e\}$ are frozen) subject to the orthonormal conditions in Eq. (4), can be obtained approximately by using the following effective Hamiltonian[4,14,23]:

$$H_{\text{clus}}^{\text{eff}} = H_{\text{clus}} + H_{\text{env}}^{\text{eff}},$$

$$H_{\text{env}}^{\text{eff}} = H_{\text{env}} - \sum_i^{N_c \text{ env}} \sum_e^{N_e/2} 2\epsilon_k |\phi_k\rangle\langle\phi_k| = \sum_i^{N_c \text{ env}} \sum_e h_e(i)$$

$$(8)$$

[the environment atomic orbitals (ϕ_k) and atomic orbital energies (ϵ_k) are used to construct the environment projector operator] and minimizing $\langle\Phi_{\text{clus}}|H_{\text{clus}}^{\text{eff}}|\Phi_{\text{clus}}\rangle$.

In order to make computations feasible, it is convenient to use the model potential approximation to represent the two-electron interactions arising from the lattice Coulomb and exchange operators J_k and K_k. This leads to the lattice model potential Hamiltonian.

$$H_{\text{clus}}^{\text{MP}} = H_{\text{clus}} + H_{\text{env}}^{\text{MP}} = H_{\text{clus}} + \sum_i^{N_c \text{ env}}\sum_e h_e^{\text{MP}}(i),$$

$$h_e^{\text{MP}}(i) = [-(Z_e - N_e)/r_{ei} + V_{\text{coul}}^e(i)]$$

$$+ [V_{\text{ex}}^e(i) + P^e(i)] = E(i) + Q(i), \quad (9)$$

where

$$-N_e/r_{ei} + \sum_{k\in e}^{N_e/2} 2J_k(i) \simeq V_{\text{coul}}^e(i),$$

$$-\sum_{k\in e}^{N_e/2} K_k(i) \simeq V_{\text{ex}}^e(i), \quad (10)$$

$$-\sum_{k\in e}^{N_e/2} 2\epsilon_k |\phi_k\rangle\langle\phi_k| = P^e(i).$$

In Eq. (9) we have separated the electrostatic potential $E(i)$ from the quantum potential $Q(i)$ consisting of exchange and projection operators. This partition facilitates the analysis of the effects of the various cluster–environment interactions.

According to Ref. 19, the electrostatic potential that collects the deviation from a point-charge approach $V_{\text{coul}}^e(i)$ may be accurately represented by

$$V_{\text{coul}}^e(i) = \sum_j A_j^e r_{ei}^{n_j^e} \exp(-\alpha_j^e r_{ei}^2)/r_{ei} \quad (11)$$

and the nondiagonal spectral representation of an operator is used for the nonlocal exchange

$$V_{\text{ex}}^e(i) = \sum_l \sum_{m=-l}^l \sum_{a,b} |alm\rangle A^e(l;a,b) \langle blm|, \quad (12)$$

where $|alm\rangle$ and $|blm\rangle$ are products of radial Gaussian primitives and spherical harmonics, l goes up to the highest angular quantum number in the set of occupied atomic orbitals on e, and a, b run over the primitives used to expand the atomic orbitals of a given l on e. The coefficients $A^e(l;a,b)$ are the elements of the matrix

$$A^e = -S^{-1}KS^{-1},$$

where

$$S_{ij} = \langle i|j\rangle \text{ and } K_{ij} = \langle i|\sum_{k\in e}^{N_e/2} K_k|j\rangle,$$

$|i\rangle$, $|j\rangle$ being functions of the set $\{|alm\rangle\}$.

In order to apply the method to a particular system, one has to decide upon which set of ions forms the cluster and which set of external ions is included in the sum Σ_{env}^e in Eq. (9). The first decision should be guided by the separability properties assumed in Eq. (1). The second decision should fulfill the requirement of convergence of the effects produced by the inclusion of more external shells of ions on the calculated properties. These aspects are analyzed in the next section.

We would like to stress that though we have assumed in the formulation that all the electrons in the cluster are treated explicitly, the use of a core model potential cluster Hamiltonian is compatible with the formalism if the core model potential Hamiltonian for the cluster is used instead of H_{clus} and the wave function Φ_{clus} is consequently factorized.

III. CALCULATIONS ON THE GROUND STATE OF NaCl:CuCl₆⁵⁻

As mentioned before, there is some experimental evidence that the Cu⁺ ions occupy on site positions in the NaCl lattice substituting Na⁺ ions.[20] However, the nature of the local geometry around the Cu⁺ ions is not clear and recent EXAFS studies[21] suggest the existence of a large lattice distortion around Cu⁺ in which some of the Cl⁻ ions are closer to the Cu⁺ than to the lattice Na⁺.

The simplest model to calculate the impurity–ligand equilibrium distance is the isolated CuCl₆⁵⁻ cluster. The values of the ground state ($^1A_{1g}$) total energy of the octahedral cluster obtained in all-electron SCF calculations at different Cu–Cl internuclear separations are presented in Table I. The results show a dissociative nuclear potential. This feature is not expected to be corrected by including correlation effects. On the other hand, the basis set used (not only for these calculations but for all those presented in this paper) is (53321/5211*/41) on Cu and (5321/521/1*) on Cl[24] and this type of basis set has proven to give equilibrium geometry

TABLE I. Results of SCF calculations on the O_h ground state of CuCl₆⁵⁻ *in vacuo*.

$r(\text{Cu}^+\text{–Cl}^-)$ (bohr)	Total energy (hartree) + 4394
5.5	− 0.094 60
5.6	− 0.110 29
5.7	− 0.124 96
5.8	− 0.138 73
5.9	− 0.151 70
6.0	− 0.163 96
6.1	− 0.175 57
6.2	− 0.186 61
6.3	− 0.197 12
6.4	− 0.207 17
6.5	− 0.216 78

TABLE II. SCF total energy of $CuCl_6^{5-}$:NaCl using the pointcharge approximation to represent the crystalline environment.

Total energy + 4397 in hartree units				
No. shells:	1	2	3	4
External ions:	118	336	722	1324
r(Cu–Cl)(bohr)				
5.4	− 0.801 583	− 0.837 450	− 0.836 418	− 0.836 628
5.8	− 0.797 827	− 0.845 226	− 0.844 027	− 0.844 241
Diff.	0.003 756	− 0.007 776	− 0.007 609	− 0.007 613

values very close to those calculated using extended basis sets for transition metal halides.[25] Therefore, the interactions of the $CuCl_6^{5-}$ with its crystalline environment must be taken into account in order to obtain a meaningful description of the impurity–ligand bonding.

In addition to the application of the formalism described in Sec. II to the calculation of the Cu–Cl distance in NaCl:Cu+, we performed some preliminary calculations corresponding to more approximate representations of the environment in order to assess their reliability as well as to make more evident the role of the different interactions collected in the environment one-electron Hamiltonian H_{env}^{MP} of Eq. (9). The calculations performed are described next. Their results are discussed together later.

The crystal structure used to locate the external Cl− and Na+ ions has been taken from Ref. 26. The Cu+ ion, which substitutes a Na+ ion, is located at the origin (0,0,0) and the unit cubic cell ($a_0 = 5.640\ 56$ Å[26]) is arbitrarily centered on it. All ions within this reference unit cell are always included in the calculations: $CuCl_6^{5-}$ as the all-electron cluster and the remainder (12 Na+ and 8 Cl−) as part of the environment. Now, we define the first *shell* as the set of ions located outside the reference unit cell and within the concentric cubic volume with edge length 2 a_0. Analogously, we define the nth shell as the set of ions included between the concentric cubic volumes whose edge lengths are $n\ a_0$ and $(n + 1)\ a_0$.

A. Point-charge approximation

Within a point-charge model of the crystalline environment, the expression for H_{env}^{MP} of Eq. (9) reduces to

$$H_{env}^{p.ch} = \sum_i^{N_c} \sum_e^{env} [- (Z_e - N_e)/r_{ei}] \qquad (13)$$

and the second and third terms in Eq. (5) reduce to

$$\sum_e^{env} \sum_c^{clus} (Z_e - N_e)Z_c/r_{ce}$$

which has to be added to the SCF energy and which varies with the geometry of the cluster.

The electrostatic potential created by the external point charges is usually evaluated through the Ewald method and an analytical representation of it inside the cluster volume is used instead of Eq. (13).[7,17] We have avoided this approximation to the proper point-charge potential. Instead, we arranged the infinite sum Σ_e^{env} by shells and studied the convergence of the total energy of $CuCl_6^{5-}$ with the number of shells added. We used fractional charges on the ions located

on the faces, edges, and corners of the cubic volume considered, according to Evjen's method,[27] so tht the shells are neutral.

The values of the total energy at r(Cu–Cl) = 5.4 bohr and r(Cu–Cl) = 5.8 bohr including 1, 2, 3, and 4 shells are collected in Table II. (hartree and bohr units are used to express energies and distances, respectively.) The calculations including three shells already show good convergence of the total energy. The addition of the fourth shell changes the value of the total energy by 2×10^{-4} hartree and, more importantly, its variation with r(Cu–Cl) by 4×10^{-6} hartree. The calculations of the total energy including three shells of point charge ions will be referred to as (300) calculations (the three numbers in parentheses indicate the number of shells on which the point-charge, charge density, and quantum effects are included, respectively, in H_{env}^{MP}).

B. Charge density approximation

Within this approximation the effect of the environment is still purely electrostatic. The deviation from the point-charge description is accurately represented by a nine-term expansion for Na+ and a ten-term expansion for Cl− [cf. Eq. (11)] (see Table III).

The expression for H_{env}^{MP} reduces now to the operator $E(i)$ in Eq. (9). Numerical analysis of the second term of Eq. (5) (attractive energy between the nuclei of the cluster and the external frozen atomic electron densities) revealed that it must be evaluated as the shown expectation value

TABLE III. Parameters of the electrostatic potential that collects the deviation from a point charge approach of Na+ and Cl− [Eq. (11)]. The linear coefficients fulfill the condition $\Sigma_j A_j^e = N_e$.

Na+		Cl−	
$- A_j$	α_j	$- A_j$	α_j
0.091 015	176 082.74	0.165 308	179 975.24
0.178 253	14 019.316	0.325 635	14 445.363
0.404 974	2 026.710 7	0.755 751	2 081.412 3
0.871 950	384.903 58	1.538 547	399.124 54
1.416 560	90.374 026	1.903 340	89.203 700
1.487 066	20.460 150	3.735 031	20.099 260
2.850 708	5.619 583 0	2.959 284	7.260 268 9
2.068 050	2.259 303 2	2.330 821	1.478 041 5
0.631 425	1.073 378 5	3.310 111	0.590 333 9
		0.976 173	0.204 276 8

All the exponents n_j^e [Eq. (11)] are set to 0

TABLE IV. SCF results for the ground state of $CuCl_6^{5-}$:NaCl.

r(Cu–Cl)(bohr)	Total energy of $CuCl_6^{5-}$ + 4397[a] in hartree units					E_{proj}/hartree
	(300)	(310)	(311)	(30P)	(31P)	(311)
4.8			− 0.419 30	− 0.163 33	− 0.214 55	0.576 89
5.0			− 0.431 92	− 0.154 69	− 0.210 27	0.620 24
5.2			− 0.429 55	− 0.128 33	− 0.188 98	0.669 40
5.4	− 0.836 42	− 0.929 65	− 0.413 16	− 0.084 56	− 0.151 15	0.726 34
5.6	− 0.843 13	− 0.947 77	− 0.381 90			0.793 03
5.8	− 0.844 03	− 0.964 04	− 0.333 27			0.871 45
6.0	− 0.840 32	− 0.981 82	− 0.263 14	0.172 00	0.081 90	0.963 10
R_e (bohr)	5.733	⩾6.0	5.067			
R_e (Å)	3.034		2.681			
$\bar{v}_e$ (cm^{-1})	125		213			

[a] The terms independent of the cluster geometry [Eq. (5)] are not included.

when e runs over the Cl$^-$ neighbors nearest to the $CuCl_6^{5-}$ cluster, otherwise the corresponding point-charge approximation is accurate.

In order to determine the convergence of the effects of the deviation from the point-charge approach, we calculated the total energy of $CuCl_6^{5-}$ including the point-charge electrostatic potential up to the third shell plus the deviations from the point-charge approach (i) on the first shell and (ii) up to the second shell. The difference between the two total energy values turned out to be 2×10^{-5} hartree at r(Cu–Cl) = 5.8 bohr. Therefore the correcting potential was used only on the first shell to calculate the $CuCl_6^{5-}$ nuclear potential. This type of calculation will be called (310).

C. Model potential approximation

Now, the representation of the crystalline environment includes also the quantum effects derived from the cluster–environment exchange and orthogonality interactions. The whole environmental one-electron Hamiltonian H_{env}^{MP} of Eq. (9) is used to describe the interaction with all ions included up to first shell. The only long-range interaction among those included in H_{env}^{MP} is the point-charge electrostatic potential; therefore, a point-charge representation of the second and third is added to ensure its convergence. These calculations will be called (311).

The basis sets, atomic orbitals, and orbital energies necessary to obtain the exchange operators [Eq. (12)] and the lattice projectors [Eq. (10)] were taken from the atomic calculations on Na$^+$ ^1S (43/4) and Cl$^-$ ^1S (433/43) of Ref. 24.

D. Results

The results of (300), (310), and (311) calculations described above are shown in Table IV and Fig. 1. The point-charge approximation (300) gives a considerably long Cu–Cl equilibrium distance R_e = 3.043 Å and a low value of the totally symmetric vibrational frequency $\bar{v}_e$ = 125 cm^{-1}. The results of our (310) calculations show the effects of the deviation from the point-charge model of the electrostatic potential. The dissociative situation observed in the *in vacuo* results arises again. Finally, the consequences of the quan-

tum effects due to the cluster–environment exchange and orthogonality interactions, as shown by the (311) calculations, are very important for this system. The final results show a bonding nuclear potential with R_e = 2.681 Å and $\bar{v}_e$ = 213 cm^{-1}.

It is interesting to compare the calculated Cu–Cl distance with that between Na and Cl in the bulk NaCl:

	Cu–Cl(311)	Na–Cl (bulk)	Cu–Cl (300)
distance (Å)	2.681	2.8203	3.034.

The local distortion due to inclusion of the impurity Cu$^+$ ion is described as an elongation of the Cu–Cl distance of 0.21 Å with respect to that of the Na–Cl in the bulk by the point-charge calculation (300), whereas a shortening of 0.14 Å is obtained when the electrostatic and quantum effects are
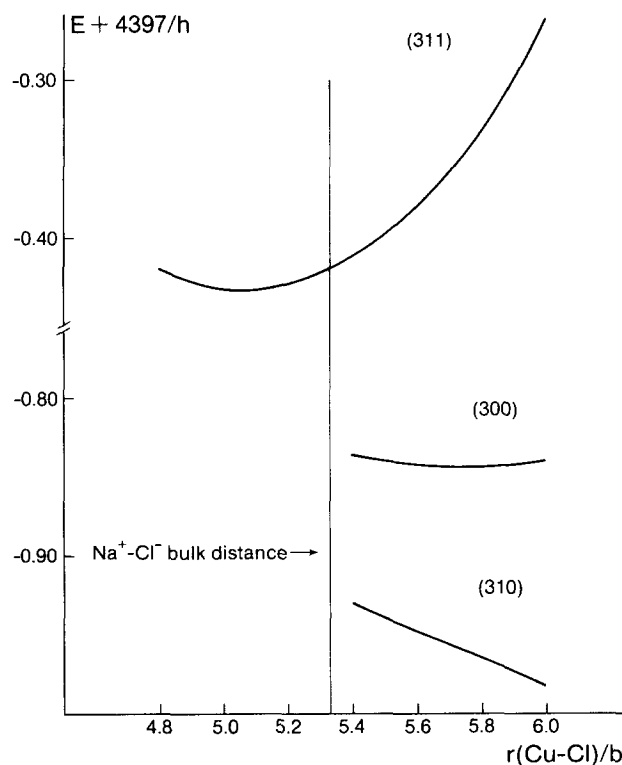

FIG. 1. Results of SCF calculations on the O_h ground state of $CuCl_6^{5-}$:NaCl.

taken into account in the calculation (311). This means that predictions of local geometry distortions resulting from the presence of impurities in a crystal may be qualitatively wrong if the cluster–lattice quantum effects are disregarded and only electrostatic effects are included in the lattice models.

The kind of distortion obtained (Cl^- moving towards Cu^+) is in qualitative agreement with the extended x-ray absorption fine structure (EXAFS) experiments.[21] However, the experiments suggest the existence of a larger distortion, including lowering of the local symmetry around Cu^+, which we have not explored. On the other hand, the calculated value of $\bar{v}_e = 213$ cm^{-1} compares fairly well with the unpublished experimental value 161.3 cm^{-1} quoted in Ref. 22; such a discrepancy is typical for results from all-electron *ab initio* RHF calculations on transition metal halides.[25] Recent RHF calculations on NaCl:CuCl$_6^{5-}$ by Winter *et al.*,[17] including lattice Na$^+$ effects through the use of complete-cation pseudopotentials and lattice Cl$^-$ anions as point charges, as well as a careful fitting of the lattice electrostatic potential inside the CuCl$_6^{5-}$ cluster, lead to $R_e = 2.819$ Å, suggesting the existence of little or no distortion around the Cu$^+$ impurity, in contrast with the results presented here.

Since the theoretical limit of the calculations presented in this paper would be reached by including shells of lattice ions on all-electron RHF calculations, we obtained an estimate of the error associated to the lattice model potential approximation by calculating the ground state of a model system which is a one-dimension replica of the NaCl:Cu$^+$ lattice:

$$Na_3^+ -Cl_2^- -Na_1^+ -Cl^- -Cu^+ -Cl^- -Na_1^+ -Cl_2^- -Na_3^+.$$
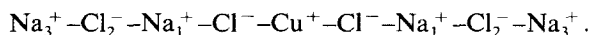
We performed two types of calculations on this system. First, we considered all the electrons on all centers except the two Cl$_2^-$ (represented as model potential centers) and the two Na$_3^+$ (represented as fractional point charges + 1/2). This calculation will be called all-electron calculation (AE). The second type differs only in that the two Na$_1^+$ were excluded from the linear cluster wave function and treated as model potential centers. This calculation [(called MP) is analogous to the three-dimensional (311)]. The equilibrium parameters associated with the totally symmetric vibration of the two Cl$^-$ are

	equilibrium distance (Å)		$\bar{v}_c$ (cm^{-1})
	Cu–Cl	Na$_1$–Cl	
AE	2.393	3.248	155 ·
MP	2.343	3.298	191
error	− 0.05	+ 0.05	36

These results reveal that, first, in the AE one-dimension lattice the Cl$^-$ is more tightly bound to the central Cu$^+$ than to the Na$^+$, in qualitative agreement with the (311) prediction for the three-dimensional lattice. Second, the discrepancies shown between the AE and MP calculations (0.05 Å for R_e and 36 cm^{-1} for $\bar{v}_e$) may be probably considered as upper bounds to the errors of the prediction of the R_e and $\bar{v}_e$ in the (311) calculations on NaCl:CuCl$_6^{5-}$ with respect to a hypothetical calculation in which the next nearest neighbors were included in the cluster. This conclusion is based on the fact that in the linear molecule the densities of the Na$^+$ ions

are expected to be more polarizable than in the highly symmetrical three-dimensional lattice and thus deviate more from the frozen-ion approximation implicit in the MP calculation.

A final set of calculations were carried out in order to assess further the relative importance of the cluster–environment interactions and their variation with the cluster geometry. The results are collected in Fig. 2. The calculations (30P) and (31P) are identical to their counterparts (300) and (310) except that now they include one shell of ion projector operators, $P^e(i)$ [Eq. (10)], and no cluster–lattice exchange effects are considered. The differences between (300) and (30P) show that the long value of the Cu–Cl distance for the point-charge lattice, R_e (300), is partly due to a collapse of the cluster wave function onto the lattice sites. It is also evident that the remaining interactions are important in order to get the final impurity–ligand equilibrium distance. Comparison of the nuclear potentials (30P) and (31P) shows the effects of the electrostatic deviation from the point-charge approximation. [Comparison between the (300) and (310) calculations is less adequate to ascertain such an effect, because the absence of lattice projectors results in collapse of the (310) cluster wave function onto the lattice sites.] These effects result from different asymptotic behavior of the point charge and the true electrostatic potentials $E(i)$ in the vicinity of the lattice nuclei: the point-charge potentials tends to $- (Z_e - N_e)/r_{ei}$, whereas $E(i)$, in Eq. (9), tends to $- Z_e/r_{ei}$, thus attracting more the cluster electronic density. Finally, the cluster–lattice exchange interactions, (31P) → (311), and their variation with the geometry of the cluster appear to be considerable, bringing about a final and important correction to the equilibrium
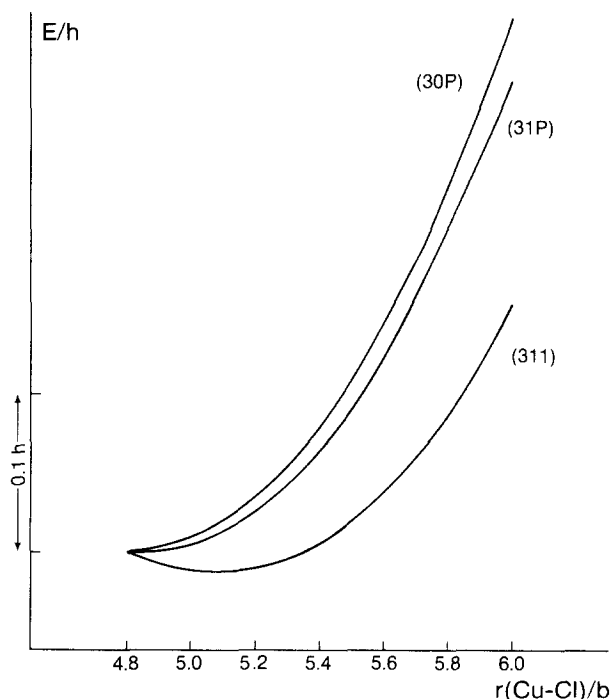

FIG. 2. Results of SCF calculations on the O_h ground state of CuCl$_6^{5-}$: NaCl. The values of the total energy have been shifted to a common origin at r(Cu–Cl) = 4.8 bohr.

geometry. This result shows that using more approximate representations of the cluster–environment exchange than the one used here (i.e., local approximations) might worsen the quality of the results in systems similar to the one studied here.

The relative importance of the quantum effects in describing the ground state energy curve of $NaCl:CuCl_6^{5-}$ shown by or calculations, clearly reveals that the cluster–environment interactions are ionic enough so that a frozen lattice approximation can be applied, but not ionic enough so that a purely electrostatic approximation can be acceptable. The variation of the overlap between the $CuCl_6^{5-}$ wave function and the external ions with the Cu–Cl distance also illustrates this departure from strong ionicity and may be seen as being responsible for the importance of the quantum interactions. This overlap can be measured by the projection energy

$$E_{proj} = \left\langle \Phi_{clus} \left| \sum_i^{N_c} \sum_e^{env} P^e(i) \right| \Phi_{clus} \right\rangle$$

and is listed in Table IV.

IV. CONCLUSIONS

In this paper we extend the use of the *ab initio* model potential method[19] to the representation of the crystalline environment in *ab initio* calculations on crystal impurities. We applied the method to the study of the local distortion on NaCl:Cu⁺. The study shows many aspects that make the MP method a useful and accurate methodological tool to study solids: the underlying basic approximation is the frozen-environment approximation; the environment one-electron potential can be easily incorporated into different types of *ab initio* molecular methods, either mono- or multiconfigurational; the (nonlocal) cluster–environment quantum interactions are represented accurately; the contributions of the lattice effects (point charge, charge density, exchange, and orthogonality) can be easily analyzed. All these characteristics, together with the simplicity of the formalism presented here, make the field of applications of the model potential method wider and, furthermore, question the usefulness of more approximate representations of the cluster–lattice interactions, such as those including only electrostatic effects.

With regard to the SCF ground state of octahedral $CuCl_6^{5-}$ embedded in the NaCl lattice, our results show that the point-charge approximation represents incorrectly the effects of the crystalline environment on the equilibrium geometry of $CuCl_6^{5-}$. As a consequence of neglecting quantum effects (exchange and orthogonality) and electrostatic effects due to the non-point-charge character of the lattice ions this approximation leads to an impurity–ligand equilibrium distance 0.45 Å too long. The impurity–ligand geometry obtained by representing the environment through a model potential formalism shows that the surrounding chlorines are more tightly bound to the Cu⁺ impurity than to the Na⁺ in the bulk. This result is in qualitative agreement with recent EXAFS measurements.[21] However, the local distortion around Cu seems to be larger,[21] including a lowering in the O_h symmetry that we have not explored. The values obtained for the Cu–Cl equilibrium distance (2.681 Å) and the

totally symmetric vibrational frequency ($213\ cm^{-1}$) are expected to be closer than 0.05 Å and $36\ cm^{-1}$, respectively, to an all-electron RHF *ab initio* calculation including the nearest neighbors to $CuCl_6^{5-}$ in the cluster wave function.

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