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Interatomic Auger rates for the sodium fluoride crystal

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Interatomic Auger rates for the NaF crystal are calculated for initial 1*s*, 2*s*, and 2*p* holes in the Na^+ ion. The crystal is simulated by a $(NaF_6)^{5-}$ cluster embedded in a large number of point ions, and the one-electron orbitals are obtained from restricted Hartree-Fock calculations of the initial state. The continuum-electron orbital is obtained from the Coulomb potential for a spherically averaged superposition of atomic charge densities for the initial state, and exchange is treated by the method of Riley and Truhlar. The continuum orbital is orthogonalized to the occupied molecular orbitals. The calculated Na(*KLL*) rate is about 20% greater than the experimental value. The calculated interatomic Auger widths for the transitions Na(1*s*)Na(2*p*)F(2*p*), Na(2*s*)Na(2*p*)F(2*p*), and Na(2*p*)F(2*p*)F(2*p*)′ [following the notation of J. A. D. Matthew and Y. Komninos, Surf. Sci. **53**, 716 (1975)] are 0.001 73, 0.641, and 0.153 eV, respectively. For comparison, the width of the Na(*KLL*) Auger transition is close to 0.26 eV. All three interatomic transitions have been identified by Citrin, Rowe, and Christman. Widths for the transitions Na(1*s*)Na(2*p*)F(2*p*) and Na(2*p*)F(2*p*)F(2*p*)′ can be inferred from experimental data. Theory and experiment agree to within 50%. This represents a considerable improvement over previous theoretical treatments.

I. INTRODUCTION

Interatomic Auger transitions were first identified in the Auger electron spectrum of LiF by Gallon and Matthew.[1] In LiF a 1*s* hole in the Li^+ ion must be filled from the valence band, which is localized predominantly on the F^- ions of the crystal. The fastest deexcitation mechanism is interatomic Auger decay involving two electrons from neighboring fluorine ions. Analogous interatomic Auger processes occur in the other alkali halides and ionic solids. The identification of the interatomic processes can frequently be made on the basis of the measured Auger electron energies. The corresponding rates, however, are not measured. Citrin[2] pointed out that interatomic Auger processes could provide an environment-dependent source of broadening which needed to be taken into account in the interpretation of x-ray photoemission (XPS) linewidths. Subsequently it was shown that broadening by coupling to lattice vibrations could account for most of the broadening of core-hole states in XPS.[3–5] From Refs. 3 and 4 it appears that approximately 0.1 eV of core-hole linewidth could be attributed to interatomic processes in the alkali halides. The size of this potential contribution to core-hole widths, compared to experimental uncertainties of about ±0.05 eV, makes the experimental determination of interatomic Auger rates difficult. For this reason the development of reliable theoretical means to evaluate interatomic Auger rates is important.[5]

Interest in the experimental consequences of interatomic Auger decay led Matthew and Komninos to undertake the first quantitative estimates of rates for the process.[6] They introduced a two-atom model and considered transitions of the form $A(x)A(y)B(z)$ and $A(x)B(y)B(z)$. Here A and B designate neighboring atoms and x,y,z designate one-electron orbitals in which holes occur. A hole occurs in x in the initial state and holes occur in y and z in the final state. The first type of transition is called an intra-inter (intra-atomic–interatomic) transition and the second type is called an inter-inter (interatomic-interatomic) transition. An Auger transition within a given atom can be called an intra-intra (intra-atomic–intra-atomic) transition. Matthew and Komninos assumed that the orbitals on neighboring atoms were essentially nonoverlapping. On this basis they then showed that the Auger matrix element for the intra-inter process reduces approximately to the product of the dipole matrix elements for the allowed optical transition $A(x)A(y)$ and the photoionization of B. Thus they expressed the intra-inter Auger rate in terms of known quantities, obtaining rates of the order of 10^{-5} a.u. or smaller. A rate of 1 a.u. is equivalent to 4.134×10^{16} sec^{-1} and to a linewidth contribution of 27.212 eV. For comparison, the *KLL* Auger rate in Na is about 0.0108 a.u., corresponding to a width of 0.29 eV; the $K\alpha$ radiative rate is 2.46×10^{-4} a.u. or 1.02×10^{13} sec^{-1}.[7] The inter-inter transitions were not discussed in detail in Ref. 6, but were estimated by replacing the dipole matrix element for the $A(x)A(y)$ transition with that for the crossover radiative transition $A(x)B(y)$. On this basis it was concluded that such matrix elements are very much less than the corresponding intra-inter matrix elements and play no important role in interatomic Auger processes.

Yafet and Watson reconsidered the intra-inter process and introduced a new approach which is conceptually very similar to the one we have adopted.[8] For the NaCl crystal they envisaged a $(NaCl_6)^{5-}$ cluster of a central

Na^+ and six Cl^- neighbor ions. From the Na^+ and Cl^- atomic orbitals (AO's), approximate cluster molecular orbitals (MO's) were constructed by using the Na AO's directly and by generating MO's of O_h group symmetry from the Cl AO's. These MO's were then orthogonalized to the ones on Na. For the continuum orbital, a plane wave was orthogonalized to the occupied MO's. Partial waves of angular momentum less than or equal to four were included and led to a lower bound of 0.788 eV for the width associated with the intra-inter transition Na(2s)Na(2p)Cl(3l). The experimental width of the 2s core hole in NaCl was reported to be of the order of 0.5 eV.[8] The inter-inter processes were not calculated in Ref. 8, but it was estimated that the width for the transition Na(2s)Cl(3s)Cl(3l) would be between 1 and 2 orders of magnitude less than that of the intra-inter process and that the width of the transition Na(2p)Cl(3p)Cl(3p) should be of the order of magnitude of ~ 0.02 eV.

Clearly the rates from this more complete theory are much larger than those estimated by Matthew and Komninos. The main cause of the discrepancy is not difficult to identify. The orthogonalization technique of Yafet and Watson leads to cluster Cl($n=3$) MO's which have non-negligible components of the Na AO's, allowing the valence electron to spend some of its time near the Na ion. As a result, close-in contributions to the interatomic Auger matrix element are included by Yafet and Watson which are completely missing in the treatment of Matthew and Komninos. For the intra-inter process, the results of Matthew and Komninos represent an estimate of the distant contributions to the interatomic Auger matrix element.

The importance of close-in contributions to the interatomic Auger matrix element makes it essential to obtain accurate charge distributions for the valence orbitals in the presence of the initial core hole. For this reason we have chosen to extend the work of Yafet and Watson by using Hartree-Fock theory to obtain the MO's of the $(NaF_6)^{5-}$ cluster, which we embed in a cubic array of point ions to simulate the NaF crystal. This should provide an adequate description of the shift in electronic charge occasioned by the creation of the Na^+ hole. As described in more detail later, we will also depart from the approach of Ref. 8 by introducing a better continuum orbital and by summing the continuum-electron partial wave expansion to convergence.

In 1978 a new motivation for studying interatomic Auger processes in ionic solids was provided by Knotek and Feibelman.[9] It was observed that in maximal valency oxides the yield of desorbed positive oxygen ions increased substantially at the lowest-energy threshold for core-hole production in the metal ions. The desorption could be initiated either by electrons or photons. Knotek and Feibelman proposed that the inter-inter process, possibly accompanied by shakeoff, could convert the negative oxygen ions into positive ones. The reversal of the Madelung potential seen by the ion could then lead to its desorption from the surface. The phenomenon of Auger-induced positive ion desorption has since been observed in a variety of circumstances, and the Knotek-Feibelman mechanism described above is generally accepted, despite some problems with the ion desorption mechanism for alkali halides.[10] According to Knotek and Feibelman, the inter-inter process must not have to compete at too much of a disadvantage with other more probable deexcitation mechanisms such as regular intra-atomic Auger decay. This competition is their explanation for the general lack of positive oxygen ion desorption in the nonmaximal-valency oxides.[11] Cation core holes in these latter oxides can decay by regular intra-intra Auger processes. The maximal valency oxides, however, resemble the alkali halides in which a core hole in the highest occupied cation level is expected to decay in interaction with the valence-band electrons, localized primarily on the anions.

Thus far, in ion desorption experiments concerning the Knotek-Feibelman mechanism, it has usually not been possible to observe the accompanying interatomic Auger electrons.[12] For this reason reliable theoretical values of rates for the inter-inter process are of particular importance. There are two types of inter-inter processes which need to be considered.[1] In process 1, the final holes occur in different anion neighbors of the initial hole-containing cation. These Auger decays do not contribute directly to the production of positive ions. In process 2, both final holes occur on the same neighbor. These are the ones of significance to the Knotek-Feibelman mechanism. Because there is of the order of 10-eV difference in the energies of the corresponding Auger electrons,[1] the two processes can be distinguished in principle. In the context of the Knotek-Feibelman mechanism, the rate for process 2 needs to be sufficiently large compared to those of potentially competing radiative and charge exchange processes.[13] In the NaF crystal, energy conservation requirements prevent the decay of a 2p hole in the Na^+ cation by process 2.[14] Thus this work will not be directly concerned with the Knotek-Feibelman mechanism.

The selection of NaF for the initial test of our theory was made because the work of Citrin, Rowe, and Christman[14] provides a comprehensive experimental study of the Auger spectrum from the creation of 1s, 2s, and 2p holes in the Na^+ ion in the NaF crystal. In addition, a quantitative value of the ratio of the Na(1s)Na(2p)F(2p) transition rate to that of the Na($KL_{23}L_{23}$) rate can be obtained from their data. Finally, a second check on the theory can be obtained from the lifetime of the Na(2p) hole state in NaF.[4] To summarize the results briefly, the agreement between theory and experiment is satisfactory, even for the inter-inter process which we have evaluated for the first time. Our results for the 2s hole intra-inter process are compatible with those of Yafet and Watson for NaCl.[8]

The necessary theory is presented in Sec. II. The results of the calculations are presented in Sec. III and summarized in Sec. IV.

II. THEORY

The theory described below is a theory of Auger processes in molecules, using the fixed-nucleus approximation. A molecular cluster embedded in point ions is used to simulate the solid. The theory of Auger processes in molecules follows that for atoms,[15] and has been the object of considerable theoretical development.[16–21] We restrict our attention to systems which have a closed-shell structure before the creation of the initial core hole. Since we are interested in obtaining reliable values for the total Auger rate for a given initial core hole, we compute the Auger matrix elements using the set of orthonormal bound-state molecular orbitals from the open-shell restricted Hartree-Fock solution for that initial core hole. For the NaF crystal we use an $(\mathrm{NaF}_6)^{5-}$ cluster embedded in a cubic array of point ions of unit charge with coordinates $(\pm la, \pm ma, \pm na)$ and $l,m,n \le 5$. Here the symbol a represents the cation-anion separation of 2.31 Å. The Hartree-Fock calculations are described elsewhere.[22] The continuum orbital is computed numerically by standard techniques from a spherical potential centered on the Na^+ ion. This spherical potential will now be defined.

The Na^+ ion is described by its atomic Hartree-Fock charge density computed either with or without a core hole, and the F^- ions are described by the atomic Hartree-Fock charge density determined from the $1s$, $2s$, and $2p$ orbitals of Huzinaga.[23] The Gaussian-type basis functions used by Huzinaga permit spherical averaging of a F-atom charge density and Coulomb potential about the central Na ion to be carried out analytically. The number of $\mathrm{F}(2p)$ electrons (36 in the ground-state cluster) can be reduced to produce continuum-orbital potentials associated with final-state $\mathrm{F}(2p)$ holes. The potential from the rest of the solid is approximated by a shell of positive charge $+5e$ situated midway between the (110) sphere and the (111) sphere. For the closed-shell ground-state cluster, the Coulomb potential vanishes outside this shell; in the case of an initial nl hole in the Na^+ ion, for example, this Coulomb potential becomes that of a unit positive charge. Given this spherically symmetric charge density and its potential, exchange is treated by the method of Riley and Truhlar.[24] The use of a spherically averaged potential greatly simplifies the calculation, at the expense of losing the inner-well resonance effects associated with the nonspherical nature of the crystal potential.[25] In the calculation of the total Auger rate, final states and continuum partial waves are summed over. This should minimize the effect of any resonances which may occur.

Once the continuum functions $Y_{lm}R_l/r$ have been computed for the partial wave (lm) as a function of the radial distance r from the origin, these functions are orthogonalized to all the bound-state MO's to produce the continuum functions ϕ_{lm} which are used in the Auger matrix elements. This orthogonalization procedure is essential to simulate the solution of the frozen-core continuum Hartree-Fock equations,[21] and because the formula we use for the Auger matrix element assumes a set of orthogonal orbitals.[15] Let us denote the core MO by ϕ_c and the valence MO's by ϕ_i and ϕ_j. In atomic units, the Auger rate P can be expressed in the form

$$P = 4\pi \sum_{l,m} \sum_{j} \sum_{i\,(\le j)} \{\delta_{ij}\,|A(clm;ij)|^2 + (1-\delta_{ij})[1.5\,|A(clm;ij) - A(clm;ji)|^2 + 0.5\,|A(clm;ij) + A(clm;ji)|^2]\} \; . \tag{1}$$

Here δ_{ij} is the Kronecker δ function and the Auger matrix element $A(clm;ij)$ is given by

$$A(clm;ij) = \int d(1) \int d(2)\, \phi_c^*(1)\phi_{lm}^*(2)(1/r_{12}) \times \phi_i(1)\phi_j(2) \; . \tag{2}$$

The factor 4π in Eq. (1) arises from the normalization of $R_l(r)$ according to

$$R_l(r) \to (k\pi)^{-1/2} \sin[kr + (Z/k)\ln(2kr) + \eta_l + \delta_l - (l\pi)/2] \; , \tag{3}$$

where η_l is the Coulomb phase shift $\arg[\Gamma(l+1-iZ/k)]$, Z is the asymptotic charge of the cluster, k is the asymptotic wave number of the electron, and δ_l is the phase shift relative to a Coulomb wave. Equations (1)–(3) are equivalent to Eqs. (1)–(6) of Ref. 16.

The evaluation of the Auger matrix element $A(clm;ij)$ is accomplished by first making single-center spherical harmonic expansions for each of the four orbitals in Eq. (2), the origin being the position of the Na ion. The expansions of the two MO's which are functions of $\mathbf{r}_1$ are then multiplied together to make the spherical harmonic expansion for a charge distribution for $\mathbf{r}_1$, following the method described by Harris and Michels.[26] An analogous expansion is made for the product of the functions of $\mathbf{r}_2$. Then the standard spherical harmonic expansion of $1/r_{12}$ is used to express $A(clm;ij)$ in terms of a sum of numerical radial integrals, as shown in Eqs. (98) and (99) of Ref. 26. In going from Eq. (98) to Eq. (99) it is necessary to include the end-point terms of the Harris-Michels integral transform.[26] The upper limit on the radial integrations was taken to be 15 a.u. A radial mesh was constructed by first extending an exponential mesh outward from the origin and then extending the same exponential mesh both outward and inward from the point $r=a$ where the F ions are located. Between the Na and F ions, and also at large r, where this mesh is too coarse for a 1-keV electron continuum wave, the mesh was replaced by a finer uniform mesh. Tests indicated that the integrals were converged to better than three parts in 10^4.

Since the Na basis functions and continuum functions are already located at the origin, it is only necessary to expand the F basis functions in terms of spherical harmonics for this origin.[27] Consider a primitive Gaussian basis function centered at (a,b,c) with respect to the origin. It is a function of the variables $(x-a,\, y-b,\, z-c)$ and is the product of a low-order polynomial in these variables and the exponential, $\exp\{-\zeta[(x-a)^2+(y-b)^2+(z-c)^2]\}$. This exponential factors into a spherically symmetrical part and an exponential which can be expanded about the origin of (x,y,z) according to the formula[28]

$$\exp[2\zeta(ax+by+cz)] \\ =4\pi\sum_{n,m} Y_{nm}(\hat{\mathbf{r}})Y^{*}_{nm}(\hat{\mathbf{a}})[\pi/(2\rho)]^{1/2}I_{n+0.5}(\rho)\ , \qquad (4)$$

where $\hat{\mathbf{a}}$ is the unit vector pointing to (a,b,c), $\rho=2\zeta r(a^2+b^2+c^2)^{1/2}$, and $I_{n+0.5}(\rho)$ is the modified spherical Bessel function. The low-order polynomial mentioned above can be expressed in terms of factors $r^pY_{pq}(\hat{\mathbf{r}})$ and multiplied into the expansion (4). Use of the addition theorem for spherical harmonics then leads directly to the required spherical harmonic expansion for a primitive Gaussian basis function centered on (a,b,c). The Hartree-Fock MO's are known in terms of linear combinations of basis functions constructed from primitive Gaussians. Thus the spherical harmonic expansion of any MO can be obtained analytically from the LCAO-MO coefficients and the basis set. This avoids the use of numerical integrations in the application of the Löwdin alpha expansion.[27] The spherical harmonic expansions are truncated at $n=n\text{max}$, where $n$max is chosen separately for each contracted Gaussian basis function. The values of $n$max were 35 for the 1s, 2s, and 2p basis functions, 25 for the 3d basis functions, and 15 for the 3s, 3p, and 4p basis functions. With these values of $n$max, the norm of the 6 F(1s) MO's is only 0.80 and the norm of the 6 F(2s) MO's is 0.984. The norm of the 18 F(2p) MO's in which we are primarily interested is 0.999. It would take $n\text{max}\sim 60$ to describe the F(1s) orbitals accurately, with no significant improvement in the precision of the Auger rates of experimental interest. All the MO's were therefore described by spherical harmonic expansions of length 35. The radial functions which appear in the spherical harmonic expansions of the MO's are complex even though the MO's are real. Because of the O_h symmetry of our cluster, canonical MO's based on polynomials in x, y, and z have radial functions which are either real or pure imaginary. For this reason the MO's obtained from the Hartree-Fock program were converted to canonical MO's, and the radial functions were stored as one-dimensional arrays. The calculations were carried out on a Cray Research Cray-XMP computer.

It can be seen from Eq. (2) that the contribution to $A(clm;ij)$ from the part of ϕ_{lm} which arises from the orthogonalization of $Y_{lm}R_l/r$ to the occupied MO ϕ_p can be expressed in terms of the electron repulsion integral $A'(cp;ij)$ obtained by replacing ϕ_{lm} by ϕ_p in Eq. (2). The required electron repulsion integrals were evaluated using post-SCF subroutines (SCF denotes self-consistent field) in the GAUSSIAN 82 program used to do the Hartree-Fock calculations.[22] As a check on the Auger matrix element program, a version of it was written to replace ϕ_{lm} by ϕ_p and calculate electron repulsion integrals directly with the same spherical harmonic expansion of the F-ion Gaussian basis functions used for the Auger matrix elements. The directly computed integrals generally agreed with those from GAUSSIAN 82 to within a few parts in 10^4. The largest discrepancy found with two parts in 10^3 for the integral $A'(1\ 18;\ 19\ 31)$ whose small absolute value, 0.000 129 6, makes its contribution to the Auger rates unimportant. Orbital 1 is the Na(1s) orbital; the others are all F(2p) MO's.

This concludes the description of our method for calculating Auger rates for molecules and we can now compare it with other approaches.[16–21] References 16 through 20 are based on the approximation of retaining only those components of the valence MO's which correspond to atomic orbitals on the atom which contained the initial core hole. This is accomplished via the LCAO-MO expansion of the MO's. Intra-atomic Auger matrix elements are then used to estimate the molecular Auger rates. We shall refer to this approximation as the local approximation. The continuum orbital in these calculations does not relate to the molecule but to the atomic process for which the intra-atomic matrix elements were obtained. Since the shape of the Auger spectrum has been the focus of attention, and not the absolute transition rate, final-state orbitals are generally used. The method is not a quantitative one unless some *a posteriori* adjustments are introduced. However, it has been a very fruitful means to analyze and correlate experimental data for a range of molecules.

The theory of Faegri and Kelly[21] is a completely *ab initio* theory, like the one presented here, and it employs a better continuum orbital. In Ref. 21, both initial- and final-state Hartree-Fock (and some configuration-interaction) calculations are carried out and used in the Auger matrix elements.[15] The small nonorthonormality effects arising from the use of both initial- and final-state orbitals in the Auger matrix element are neglected.[29] This work suggests that *ab initio* approaches for molecules can lead to results of similar accuracy to those obtained for atoms. For total Auger rates this places the accuracy in the range 20–40 %.[30–32] We believe this to be true of the approach described here, because the effects neglected in our treatment[32] tend to redistribute the Auger rates among the final states and have a smaller influence on the total Auger rate.

In our present application to interatomic Auger rates in ionic solids, an additional source of error is present. We do not know how accurately our cluster calculation approximates the results of the corresponding initial-state hole calculation in the solid. As discussed in Ref. 22, such states are known to be quite localized in the alkali halides, and this suggests that a cluster approach should be valid. The comparisons with experiment made in the next section constitute a first step in exploring the limits of the theory.

III. THE RESULTS

In Sec. II the theory and the main checks on its numerical precision were described. In this section the final results will be presented. Then a number of studies undertaken to explore the validity of the final results will be described. Some of these bear on the earlier theories in an interesting way.

A few additional words must be said about the continuum orbitals ϕ_{lm}. In his work on atomic Auger processes, McGuire[30] found that Hartree-Fock-Slater potentials containing a core hole produced rates which agreed best with experiment. The particular shell in which the hole occurred was of secondary importance. A Latter correction[33] to the potential caused the asymptotic charge Z seen by the electron to be equal to two electronic charges. For this reason, except where noted, our continuum calculations were carried out with a potential corresponding to a $2p$ hole in the Na^+ ion and one electron missing from the F($2p$) band. This results in $Z=2$. A "true" initial-state potential in our model would have an nl hole in the Na^+ ion, no electrons missing from the F($2p$) band, and $Z=1$. Calculations carried out with this and other continuum potentials will also be described. The results are not very sensitive to the precise choice of potential within our basic approximation. Experimental values were used for the Auger electron energies.

Besides the potential sensitivity of the Auger rates to the choice of continuum orbital, we were concerned about the sensitivity of the results to our choice of Gaussian basis set. For interatomic Auger processes, the polarization of the F($2p$) valence orbitals by the Na^+ core hole will move valence charge closer to the cation, with a concomitant increase in the Auger matrix element. Therefore some transitions were calculated with two basis sets, *A* and *B*. These are described in Ref. 22. Briefly, basis *A* is expected to be an adequate basis and basis *B* is expected to be a better one with more flexibility for possible shifts in the valence charge.

Naturally, our first calculations were for the intra-atomic Na(KLL) transition. Both basis sets *A* and *B* yielded a total rate of 121×10^{-4} a.u. This is larger than the values, 97.1 and 106.2×10^{-4} a.u., obtained using Hartree-Fock-Slater orbitals in Refs. 29 and 30, respectively. In the related case of neon, Hartree-Fock orbitals also lead to rates about 20% higher than Hartree-Fock-Slater orbitals.[32] The experimental rate is close to 101×10^{-4} a.u. The use of a $1s$ core hole for the continuum potential or the removal of the F($2p$) hole to make $Z=1$ changed the rate by at most 2%.

Table I exhibits the results for the interatomic Auger rates in NaF. The pattern of relative intensities is consistent with the lines observed by Citrin, Rowe, and Christman. In Table I, the notation F($2p$)F($2p$)′ indicates that the final-state holes are located on two different neighboring F ions, and not on the same ion. A transition leaving both holes on the same F ion would require about 10 eV more energy, and is energetically forbidden. To describe these final states correctly, a configuration-interaction treatment of our independent-particle two-hole states would be necessary. In calculating the Na($2p$)F($2p$)F($2p$)′ rate, we summed over all 630 independent-particle two-hole final space and spin states. Thus we included contributions from the 90 states which correspond to two holes on the same fluorine ion. Therefore, in the crudest approximation of just counting states, our sum is about 17% too high. Experimental rates for two of the transitions can be obtained from the literature. The good agreement should lend credence to theoretical predictions for the more typical systems where no experimental data are available. Our rate for the transition Na($2s$)Na($2p$)F($2p$) is in harmony with that of Yafet and Watson for the analogous transition in NaCl.

Tables II–IV allow the rates to be analyzed in more interesting detail. The first row of Table II shows that 24 continuum partial waves were required for the F($1s$) final state. In principle, the partial wave contributions need to be summed until the continuum wave function's classical turning point passes the outer boundary radius, R_o, of the fluorine orbitals in the matrix element. Then, for a continuum electron wave number k, the maximum value of l is about equal to kR_o. The next four rows show, however, that only two partial waves are required for the F($2s$) and F($2p$) final states. The contributions from the larger l values are extremely small. These results show that if an F(nl) MO has a small component on the Na ion in the LCAO-MO sense, an Auger rate involving this orbital and an initial Na^+ hole can be greatly enhanced. The Na s and p orbital require $l\leq2$ in the Auger matrix element, and the second and fourth rows of Table II contain the contributions from these small components of the F($2s$) and F($2p$) MO's. The contributions from larger l in the third and fifth rows are of the same order of magnitude as the F($1s$) rate in the first row. These rates are representative of the distant interactions discussed by Matthew and Komninos and

TABLE I. Interatomic Auger rates for the NaF crystal. Numbers enclosed in square brackets denote powers of ten by which rates are to be multiplied.

Transition	Energy (eV)	Theory rate (a.u.)	Experiment rate (a.u.)
Na($1s$)Na($2p$)F($1s$)	347	0.59[−7]	
Na($1s$)Na($2p$)F($2s$)	1003	0.71[−5]	
Na($1s$)Na($2p$)F($2p$)[a]	1023	0.637[−4]	0.82[−4][b]
Na($2s$)Na($2p$)F($2p$)[a]	16	2.36[−2]	
Na($2s$)F($2p$)F($2p$)′	40	0.141[−3]	
Na($2p$)F($2p$)F($2p$)′[a]	7	0.557[−2]	<0.37[−2][c]

[a] Observed by Citrin, Rowe, and Christman.

[b] From ratio of areas of line P_4 and Na($KL_{2,3}L_{2,3}$) line in Fig. 8 of Ref. 14 (ratio equals 0.012), together with $KL_{2,3}L_{2,3}$ rate from Ref. 31.

[c] Based on an upper bound of 0.1 eV as inferred from Table I of Ref. 4.

TABLE II. Interatomic Auger rates for a Na(1s) core hole.

Transition	Energy (eV)	Basis[a]	Range of partial wave l	Theory rate (a.u.)
Na(1s)Na(2p)F(1s)	347	A	0–24	0.59[−7]
Na(1s)Na(2p)F(2s)	1003	A	0–2	0.71[−5]
Na(1s)Na(2p)F(2s)		A	3–55	0.84[−7]
Na(1s)Na(2p)F(2p)	1024	A	0–2	0.668[−4]
Na(1s)Na(2p)F(2p)		A	3–56	0.73[−7]
Na(1s)Na(2p)F(2p)		B	0–2	0.637[−4]
Na(1s)Na(2p)F(2p)[b]		B	0–2	0.637[−4]
Na(1s)Na(2p)F(2p)[c]		A	0–2	0.092[−4]
Na(1s)F(2s)F(2p)[c]		A	0–2	0.434[−4]

[a] See the text and Ref. 22.

[b] Rate summed only over valence MO's of A_{1g} and T_{1u} symmetry.

[c] Orbitals from ground-state Hartree-Fock solution. Na(2p) and F(2s) orbitals degenerate and hybridized.

agree in order of magnitude with their theory.[6] The sixth row of Table II shows that the use of basis B leads to a slightly smaller rate. This is consistent with the somewhat more diffuse character of the valence MO's from basis B.[22] The next row of Table II considers the effect of valence orbital components on the central Na ion by summing the rate only over those valence MO's which can mix with the Na AO's, namely those of A_{1g} and T_{1u} symmetry. The contributions of the other F(2p) MO's, which have E_g, T_{1g}, T_{2u}, and T_{2g} symmetry, are omitted. It is seen that the contributions of the nonmixing MO's are indeed negligible, in agreement with the idea that the Auger process is localized around the atom with the initial core hole.[16–20]

The last two rows of Table II were obtained using ground-state MO's. As described in Ref. 22, the Na(2p) and F(2s) MO's are hybridized in the ground state. By summing over all these nearly degenerate final states, we obtain a total rate of 0.526×10^{-4} a.u. This smaller value compared to that in the fourth row is consistent with the shift in valence charge produced by the presence of the Na$^+$ core hole.

Table III concerns transitions from an initial Na$^+$(2s) hole. The first two rows show that $l\leq2$ no longer exhausts the Auger rate. Rows 3–6 exhibit the nature of the convergence of the sum over partial waves. The F(2p) MO's contain the O_h group representations T_{2u} and T_{1g}, whose spherical harmonic expansions in Y_{nm} begin with $n=3$ and $n=4$, respectively. These MO's cannot mix with the Na$^+$ A_{1g} and T_{1u} AO's. Thus, for larger l, we expect contributions which involve only the distant interactions. The seventh row gives the rate summed only over the valence orbitals of A_{1g} and T_{1u} symmetry. Of the tabulated rate, 1.769×10^{-2} a.u. comes from $l\leq2$. Since the Na MO's contain components on the F ions, all the MO's in the Auger matrix element have terms from Eq. (4) with large n. This makes it impossible to equate exactly the contributions to the rate from $l\leq2$ with those from MO's of A_{1g} and T_{1u} symmetry.

TABLE III. Interatomic Auger rates for a Na(2s) core hole.

Transition	Energy (eV)	Basis[a]	Range of partial wave l	Theory rate (a.u.)
Na(2s)Na(2p)F(2p)	16	A	0–2	1.853[−2]
Na(2s)Na(2p)F(2p)		A	3–9	0.504[−2]
Na(2s)Na(2p)F(2p)		A	0–4	2.142[−2]
Na(2s)Na(2p)F(2p)		A	0–6	2.306[−2]
Na(2s)Na(2p)F(2p)		A	0–8	2.355[−2]
Na(2s)Na(2p)F(2p)		A	0–9	2.357[−2]
Na(2s)Na(2p)F(2p)[b]		A	0–9	1.936[−2]
Na(2s)F(2p)F(2p)′	40	A	0–2	0.716[−4]
Na(2s)F(2p)F(2p)′		A	0–13	0.141[−3]
Na(2s)F(2p)F(2p)′[b]		A	0–13	0.892[−4]
Na(2s)F(2p)F(2p)′[c]		A	0–13	0.435[−4]

[a] See the text and Ref. 22.

[b] Rate summed only over valence MO's of A_{1g} and T_{1u} symmetry.

[c] Orbitals from ground-state Hartree-Fock solution.

TABLE IV. Interatomic Auger rates for a Na(2p) core hole.

Transition	Energy (eV)	Basis[a]	Range of partial wave l	Theory rate (a.u.)
Na(2p)F(2p)F(2p)′	7	A	0–7	0.648[−2]
Na(2p)F(2p)F(2p)′		A	0–2	0.444[−2]
Na(2p)F(2p)F(2p)′[b]		A	0–7	0.408[−2]
Na(2p)F(2p)F(2p)′		B	0–7	0.564[−2]
Na(2p)F(2p)F(2p)′		B	0–2	0.418[−2]
Na(2p)F(2p)F(2p)′[c]		B	0–7	0.557[−2]
Na(2p)F(2p)F(2p)′[d]		B	0–7	0.440[−2]

[a] See the text and Ref. 22.

[b] Rate summed only over valence MO's of A_{1g} and T_{1u} symmetry.

[c] Initial-state continuum function, $Z=1$.

[d] Final-state continuum function, no core hole, two valence holes.

The first four rows concern an inter-inter transition not observed by Citrin, Rowe, and Christman. Only half the rate is included in $l \leq 2$. The third row for this transition gives the rate summed only over the A_{1g} and T_{1u} valence orbitals. Distant interactions are clearly important here. The last line gives the rate computed with ground-state orbitals. The rate is only one-third of that computed from the Na$^+$(2s) initial-state orbitals.

Table IV concerns an initial 2p hole. It can be seen that approximately 65% of the converged rate (at $l=7$) comes from $l \leq 2$, or from the valence orbitals of A_{1g} and T_{1u} symmetry. The rates from basis B are lower than those from basis A. The last two rows show a lowering of the rate when successively less attractive continuum-orbital potentials are used. The rate from the initial-state potential was used as our final result in Table I. The last row is included because the use of initial-state valence MO's and final-state core and continuum MO's would occur in a ΔSCF approach to the Auger rate.[21] However, as mentioned earlier, the proper treatment of the final states should also involve the separation of the state with holes on different neighbors from those with the two holes on the same neighbor. In view of the experimentally determined upper bound of about 0.37×10^{-2} given in Table I, the lowering of the rate through the use of a final-state continuum function is worth noting.

IV. SUMMARY AND DISCUSSION

The preceding sections have shown that the standard quantitative theory of Auger decay can be successfully applied to the intra-atomic and interatomic transitions in the NaF crystal, when the crystal is simulated by a $(NaF_6)^{5-}$ cluster embedded in point ions. The use of initial-state molecular orbitals and an approximate, but carefully constructed continuum orbital, leads to rather good agreement with the available experimental data. The new features of the work reported here are the use of Hartree-Fock molecular orbitals for interatomic calculations, the use of an improved continuum function, and an essentially exact evaluation of the matrix elements and rates. The inter-inter process was treated for the first time. It should now be possible to apply the theory to other systems with some confidence.

The material presented in Sec. III has shown that the current view of the Auger process in solids[34] and molecules[16–20] as being localized on the atom with the initial core hole has to be amended if the initial level is not sufficiently deep. Naturally, shallow initial holes go with interatomic transitions. From Tables III and IV it can be seen that the contributions to the rates of the 16- and 7-eV transitions from "distant" interactions are 0.421×10^{-2} a.u. and 0.240×10^{-2} a.u., respectively. These rates correspond to linewidth contributions of about 0.1 eV, which should be observable.[5] In the context of the general theory of molecular Auger decay, our work provides a warning to the effect that a quantitative treatment of the relative strengths of the lines in a spectrum may require the inclusion of the distant contributions to the Auger matrix elements as well as the use of accurate final-state[16–21] and initial-state[35] configuration-interaction wave functions.

An important finding of our work is that the distant contributions to the interatomic rate, while quantitatively significant, are not dominant. Indeed, it appears that the local approximation can be used even on interatomic transitions for the purpose of obtaining correct order-of-magnitude rates. The local approximation was developed in the context of K-shell holes, where its validity is not difficult to believe, especially since the work of Mathew and Komninos. Our study of the shallow 2s and 2p holes shows that the local approximation can also be used for estimates in these and similar cases.

In conclusion, we return to the Knotek-Feibelman mechanism. In this context our most important result is that the inter-inter rate for the initial Na*(2p) hole is not extremely small, but is of the size of the upper bound found experimentally. A rate of 0.557×10^{-2} a.u. corresponds to 2.3×10^{14} transitions/sec. This is fast compared to the rates to be expected for competing radiative transitions and to the longitudinal-optical frequency 1.3×10^{13} vibrations/sec. As mentioned earlier, the production of positive ions by this mechanism is energetically forbidden in NaF. However, the size of the rate suggests that in other ionic systems the inter-inter step in the Knotek-Feibelman mechanism can occur with sufficient probability to make the mechanism competitive with alternative channels for energy transfer.

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