Calculated Auger transition rates for HF

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We report *ab initio* calculations of Auger transition rates for hydrogen fluoride, using Hartree-Fock molecular orbitals from finite-basis Slater-type-orbitals calculations. Continuum orbitals are calculated as spherical waves in the single-center expanded-molecular potential. Results show reasonable agreement with experiment and with previous calculations for neon. The effect of final-state configuration mixing is discussed, as well as the use of perturbation theory for improving the continuum orbitals.

I. INTRODUCTION

Auger processes have in the past provided an interesting testing ground for various theoretical treatments of atomic structure.[1] Recently, molecular Auger processes have received increasing attention due to advances in experimental techniques as well as in the theoretical treatment of molecules.[2-12] Quantitative calculations for these processes have been restricted to transition energies. Transition rates have been estimated either by comparison with isoelectronic atomic systems[6,7,9] or from population analyses combined with the use of atomic matrix elements.[3] *Ab initio* calculations of transition rates have foundered on the lack of a convenient description of the continuum orbitals of the outgoing electron.

In this paper we present calculations for Auger transition rates of hydrogen fluoride. Molecular orbitals for singly and doubly ionized states, and also transition energies, have been obtained from separate Hartree-Fock calculations. In the calculation of transition rates we have used continuum orbitals obtained as spherical waves in a single-center expanded molecular potential. This type of continuum orbitals has been used successfully previously in the calculation of the photoionization cross section for H_2.[13] HF is particularly suited for this type of calculation as it is well described in a single-center approximation. Also, the similarity between Auger processes in HF and Ne, as noted in previous investigations,[14,19] offer the opportunity of comparing the molecular calculations with high quality calculations for the isoelectronic atom.[15]

The theoretical and numerical background for the calculations as well as lowest-order results is described in the first part of this paper. The following section discusses configuration mixing in the doubly ionized final state, particularly with regard to $^1\Sigma^+$ states. Finally, we discuss the possible improvements in the description of the continuum orbitals by use of perturbation

theory and show the effect of this for two of the transitions.

All calculations presented here have been carried out at a fixed internuclear distance of 1.7328 a.u.

II. LOWEST-ORDER TRANSITION ENERGIES AND RATES

A. Transition energies

The electronic ground-state configuration of HF is $1\sigma^2 2\sigma^2 3\sigma^2 \pi^4 (^1\Sigma^+)$. K-LL Auger transitions take place between the state with a 1σ hole and the possible final states with two electrons missing from the 2σ, 3σ, and 1π orbitals. The transition energies have been discussed previously both in a limited configuration interaction (CI) calculation[5] and in an extensive Hartree-Fock study using Gaussian-type orbitals (GTO).[9] For this calculation we have recalculated the transition energies using a basis of Slater-type orbitals (STO) given by Cade and Huo,[16] enabling us to use the single-center expansion formalism for STO.[17] The program used by us for this part of the calculation consists of an STO integral program[18] combined with the UIBMOL SCF program.[6] We find that the STO transition energies as well as the total state energies differ very little from those obtained using an extended GTO basis (Table I). For the transition energies, basis set deficiencies tend to cancel when the two total energies are subtracted. The largest discrepancy between the GTO and STO calculations appears for the transition energy to the $2\sigma^1 3\sigma^1 (^1\Sigma^+)$ state with a shift of 1.4 eV. The problems involved in restricted Hartree-Fock calculations[19] for states of this type, i.e., singlet states with two holes of the same symmetry, have been discussed elsewhere.[20] The total energies for this state were obtained using orbitals optimized self-consistently for the $2\sigma^1 3\sigma^1 (^3\Sigma^+)$. Agreement with experiment is seen to be somewhat worse for the STO basis; some of this discrepancy can possibly be removed

TABLE I. Total energies and transition energies for HF.

State	Total energies (a.u.)		Auger transition energies (eV)	
	GTO basis [a]	STO basis	STO basis	Experiment [b]
$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 (^1\Sigma^+)$	-100.0583	-100.0704		
$1\sigma^1 (^2\Sigma^+)$	-74.5878	-74.5985	693.09 [c]	694.25 [c]
$1\pi^2 (^3\Sigma^-)$	-98.4140	-98.4236	648.28	
$1\pi^2 (^1\Delta)$	-98.3056	-98.3152	645.33	644.28
$3\sigma^1 1\pi^3 (^3\Pi)$	-98.2952	-98.3005	644.99	
$1\pi^2 (^1\Sigma^+)$	-98.1994	-98.2091	642.44	642.35
$3\sigma^1 1\pi^3 (^3\Pi)$	-98.1805	-98.1896	641.91	
$3\sigma^0 (^1\Sigma^+)$	-98.0005	-98.0072	636.95	636.92
$2\sigma^1 1\pi^3 (^3\Pi)$	-97.5318	-97.5495	624.50	625.1
$2\sigma^1 3\sigma^1 (^3\Sigma^+)$	-97.4141	-97.4298	621.25	
$2\sigma^1 1\pi^3 (^1\Pi)$	-97.1662	-97.1852	614.59	616.2
$2\sigma^1 3\sigma^1 (^1\Sigma^+)$	-97.0810	-97.0402	610.64	614.1
$2\sigma^0 (^1\Sigma^+)$	-96.3270	-96.3646	592.25	595.6

[a] Extended Gaussian basis (Ref. 9).
[b] Reference 14.
[c] 1σ ionization potential (Ref. 14).

by using a Fock operator specially formulated for orthogonality constrained calculations.[20]

The $2\sigma^0(^1\Sigma^+)$ transition energy shows a shift of 0.74 eV in going from the GTO to the STO basis (improved agreement with experiment). However, a differential shift between calculations and experiment, resulting in progressively poorer agreement in going from high to low energies, is present also in the STO calculations as in previous GTO calculations for HF, NH_3, and H_2O.[4,5,7,9] This supports the view that this discrepancy is not a basis set effect, but must be ascribed to correlation and geometry distortions.

B. Calculation of continuum orbitals

The orbitals calculated in the restricted Hartree-Fock calculations described above were expanded about the F atom. An STO centered on the H atom is represented as a linear combination of spherical harmonics:

$$\chi(r_H, \theta_H, \phi) = \sum_{l=|m|}^{\infty} V_l(r_F) Y_{lm}(\theta_F, \phi). \tag{1}$$

Here $V_l(r_F)$ is a function related to the modified spherical Bessel function by a set of recurrence relations.[17] In the present calculations, the sum over l was truncated at $l=18$ for σ orbitals and at $l=17$ for π orbitals.

From these single-center expanded orbitals and a multipole expansion of the H nuclear charge, we form a single-particle Hamiltonian for the continuum orbital. The orbitals are coupled to a state of correct symmetry, and for a heteronuclear diatomic molecule the orbital will be characterized by its m quantum number, the only good quantum

number for the symmetry. This Hamiltonian can now be partitioned using the set of spherical harmonics centered on F such that

$$h(r, \theta, \phi) = \sum_{l,l'} |l,m\rangle\langle l,m|h|l',m\rangle\langle l',m|$$

$$= \sum_{l} |l,m\rangle h_{ll}(r)\langle l,m|$$

$$+ \sum_{l,l'}' |l,m\rangle h_{ll'}(r)\langle l',m|$$

$$= h^0 + h', \tag{2}$$

where the bracketed expressions imply integration over θ and ϕ, and the prime on the second summation excludes the case $l=l'$. For an atom the second sum will vanish, as the spherical harmonics are eigenfunctions of h. For a diatomic this sum must be retained, but if HF is regarded as an atomic system perturbed by an off-center charge, h' may be neglected as a reasonable first approximation in calculating continuum states.

For a given energy ϵ of the outgoing electron, we now have a continuum orbital $R_\epsilon(r)|l,m\rangle$ determined by the equation

$$h^0 R_\epsilon(r)|l,m\rangle = |l,m\rangle h_{ll}(r)R_\epsilon(r)$$

$$= \epsilon R_\epsilon(r)|l,m\rangle. \tag{3}$$

This differential equation is solved by standard numerical methods; because of exchange terms in $h_{ll}(r)$, the solution must be found iteratively. For one m quantum number, there are in principle infinitely many solutions corresponding to

TABLE II. Calculated transition rates for $K\text{-}LL$ Auger transitions in HF and Ne.[a]

| HF state | Hartree–Fock transition rates (10^{-3}a.u.) | | | Correlated rates (10^{-3} a.u.) | | Ne state |
	HF	Sum HF [b]	Ne [c]	Ne [d]	
$1\pi^2(^3\Sigma^-)$	0.0	0.021	0.0	0.0	^3P
$3\sigma^1 1\pi^3(^3\Pi)$	0.021				
$1\pi^2(^1\Delta)$	1.986				
$1\pi^2(^1\Sigma^+)$	0.594	4.272	5.685	5.198	^1D
$3\sigma^1 1\pi^3(^1\Pi)$	1.692				
$3\sigma^0(^1\Sigma^+)$	0.564	0.564	0.456	0.864	^1S
$2\sigma^1 1\pi^3(^3\Pi)$	0.574				
$2\sigma^1 3\sigma^1\,(^3\Sigma^+)$	0.302	0.676	0.789	0.502	^3P
$2\sigma^1 1\pi^3(^1\Pi)$	1.288	1.930	2.034	1.396	^1P
$2\sigma^1 3\sigma^1(^1\Sigma^+)$	0.642				
$2\sigma^0(^1\Sigma^+)$	0.983	0.983	0.951	0.488	
Total	8.646	8.646	9.914	8.448	

[a] In this table HF transitions are ordered by correspondence to the Ne transition and not by decreasing energy.
[b] Sum of terms corresponding to one Ne transition.
[c] Reference 15.
[d] Reference 15. All correlations through first order.

different l values. For the present calculation only the first few of these were considered. We have generated continuum oribtals up to $l=4$, but their importance is rapidly diminishing for higher l, and no orbital with l quantum number higher than 2 contributes significantly to the Auger transition rate for HF. The continuum orbitals are normalized such that

$$R\epsilon_\epsilon(r) = (1/r)\cos[kr + \delta_l + (q/k)\ln 2kr$$
$$-\tfrac{1}{2}(l+1)\pi], \qquad (4)$$

where $k = \sqrt{2\epsilon}$.

C. Transition rates

With the normalization in Eq. (4) the Auger rate is[21]

$$P = (4/k)\left|\langle\psi_f|\sum_{m<n}v_{mn}|\psi_i\rangle\right|^2 \qquad (5)$$

where ψ_f and ψ_i are the final and initial states, respectively. The problems arising from the use of nonorthogonal orbitals optimized in separate self-consistent field (SCF) calculations have recently been discussed in relation to the Auger transitions in neon.[22] In the present case orthogonalities between different orbitals from different states are reasonably good. Overlaps between different orbitals are less than 0.007, except for $\langle 2\sigma|3\sigma\rangle$. This overlap integral is less than 0.04 for all final states except $3\sigma^1 1\pi^3(^3\Pi)$ (which has a very small transition rate) and $2\sigma^0(^1\Sigma^+)$ where the overlaps are 0.075 and 0.088, respectively. We estimate that the error arising from the use of Eq. (5) for the transition rates should be less than 9% for all final states (with

the possible exceptions mentioned above). By comparison with the calculation of transition rates in Ne, this is in all cases considerably less than the correlation contribution to the rates.[15] Our error estimates are consistent with the conclusions reached by Howat et al.[22] for Ne.

Calculated Auger transition rates are shown in Table II, where Hartree-Fock results for Ne are listed for comparison. The transition to the $1\pi^2(^3\Sigma^-)$ state is not allowed because this state cannot be coupled to one continuum orbital to give a $^2\Sigma^+$ state. The other hydrogen-fluoride Auger transition corresponding to the forbidden $2p^4(^3P)$ transition in Ne is to the $3\sigma^1 1\pi^3(^3\Pi)$ state. For the diatomic this is not forbidden, but the transition rate is proportional to

$$|\langle 3\sigma 1\pi|v|1\sigma k\pi\rangle - \langle 3\sigma 1\pi|v|k\pi 1\sigma\rangle|^2, \qquad (6)$$

where $k\pi$ is a continuum orbital of π symmetry. In the atomic limit (3σ and $1\pi\to 2p$) this quantity vanishes. In hydrogen fluoride the transition rate is very small, and is due mainly to the k_p channel (outgoing continuum orbital with p symmetry, i.e., $l=1$), while the two matrix elements involving the kd channel cancel almost completely in Eq. (6).

The group of transitions corresponding to the dominant $2p^4(^1D)$ transition in Ne also dominates the HF Auger spectrum. However, the rates are not in the statistical 2:2:1 ratio for the Δ,Π,Σ transitions, indicating the possible error in the simple model used previously for obtaining intensities.[9] The sum of the rates in this group (4.272×10^{-3} a.u.) shows the greatest absolute difference from the corresponding Ne transitions

TABLE III. Contribution to Auger transition rates in hydrogen fluoride from different outgoing channels. [a]

Final state	Partial rates (10^{-3} a.u.)			Total rate (10^{-3} a.u.)
	ks	kp	kd	
$1\pi^2(^1\Delta)$			1.986	1.986
$3\sigma^1 1\pi^3(^3\Pi)$		0.021	0.0	0.021
$1\pi^2(^1\Sigma^+)$	0.262	0.0	0.332	0.594
$3\sigma^1 1\pi^3(^1\Pi)$		0.049	1.643	1.692
$3\sigma^0(^1\Sigma^+)$	0.067	0.040	0.457	0.564
$2\sigma^1 1\pi^3(^3\Pi)$		0.574	0.0	0.574
$2\sigma^1 3\sigma^1(^3\Sigma^+)$	0.0	0.269	0.033	0.302
$2\sigma^1 1\pi^3(^1\Pi)$		1.265	0.023	1.288
$2\sigma^1 3\sigma^1(^1\Sigma^+)$	0.115	0.516	0.011	0.642
$2\sigma^0(^1\Sigma^+)$	0.975	0.013	0.0	0.983

[a] No outgoing channel with l greater than 2 contributes in lowest order.

$(5.685 \times 10^{-3}$ a.u.). This decrease of 1.4×10^{-3} a.u. relative to Ne is essentially the difference between the total Auger rates for HF and Ne $(1.3 \times 10^{-3}$ a.u.). Transition rates to other final states are in reasonable agreement with the corresponding Ne results.

Table III summarizes the contributions to the total transition rates from the different partial channels. The fact that one channel accounts for more than 80% of the transition rate in all transitions except $1\pi^2(^1\Sigma^+)$, supports a view of the K-LL Auger transition in HF as a largely atomic effect and also explains the relative success of simple intensity estimates from the Ne spectrum.[9] The one exception of this one-channel behavior $[1\pi^2(^1\Sigma^+)]$ has sizable contributions both from the ks and kd channels. Unfortunately, the peak corresponding to this transition is not resolved in the HF Auger spectrum recorded by Shaw and Thomas.[14] A bar spectrum based on the relative HF transition rates (Fig. 1) appears to give a reasonable approximation to the experimental data. However, for Ne most Hartree-Fock transi-
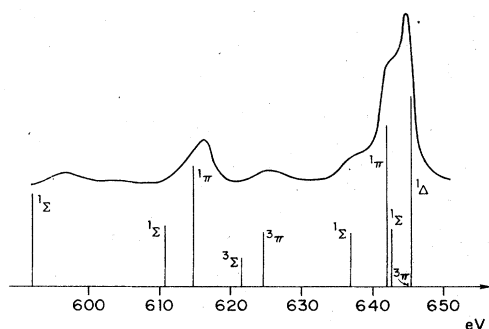

FIG. 1. Bar spectrum based on relative transition rates. The experimental spectrum (Ref. 14) is included for comparison. Note that the experimental spectrum is shifted up from the zero level for clarity. Also, experimental intensities are in arbitrary units.

tion rates are changed appreciably by correlation effects,[15] and one might expect that this will be the case also for HF.

III. FINAL-STATE CONFIGURATION MIXING

Previous studies of K-LL Auger transition rates in atoms have shown the importance of accounting for the mixing of the $2s^0 2p^6(^1S)$ and the $2s^2 2p^4(^1S)$ configurations.[23,24] Analogous mixing occurs between $^1\Sigma^+$ states in HF, but because of the lower symmetry there are now four possible states that can mix: $1\pi^2(^1\Sigma^+)$, $3\sigma^0(^1\Sigma^+)$, $2\sigma^1 3\sigma^1(^1\Sigma^+)$, and $2\sigma^0(^1\Sigma^+)$. The two $\sigma^0(^1\Sigma^+)$ states correspond to the ^1S states for Ne, while the $1\pi^2(^1\Sigma^+)$ and the $2\sigma^1 3\sigma^1(^1\Sigma^+)$ are the $M=0$ components of the $2s^2 2p^4(^1D)$ and $2s^1 2p^5(^1P)$ states. We have calculated the mixing between these four $^1\Sigma^+$ states by diagonalizing the full molecular Hamiltonian. To avoid nonorthogonality problems we have used the orbitals optimized for the $2\sigma^1 3\sigma^1(^3\Sigma^+)$ state for all four states. The calculated coefficients shown in Table IV indicate a significant mixing between all four states. The mixing between the $1\pi^2(^1\Sigma^+)$ and $3\sigma^0(^1\Sigma^+)$ states, which do not mix in the atomic case, is especially notable. The possible mixing of these two states, facilitated by the lower symmetry and the small energy separation in the molecule, was pointed out by Shaw and Thomas.[14]

The only Auger transition energy appreciably affected by the configuration mixing is that for the $2\sigma^0(^1\Sigma^+)$ state. The total energy for this state is higher than before, which is to be expected as this state is mixed only with states of lower energy. The transition rates are, however, more sensitive to configuration mixing than the energies as shown in Table V. The rate for transition to $2\sigma^0(^1\Sigma^+)$ is reduced from 0.983×10^{-3} to 0.771×10^{-3} a.u., in excellent agreement with the

TABLE IV. Total energies, configuration mixing coefficients, and transition energies for the $^1\Sigma^+$ final states from limited CI calculation.

| Main configuration | Total energies (a.u.) | Configuration mixing coefficients | | | | Auger transition energies (eV) | |
		$1\pi^2$	$3\sigma^0$	$2\sigma^1 3\sigma^1$	$2\sigma^0$	CI	Hartree–Fock
$1\pi^2(^1\Sigma^+)$	−98.2493	0.9680	0.2232	0.0448	0.1056	643.53	642.44
$3\sigma^0(^1\Sigma^+)$	−98.0122	−0.2084	0.9660	0.0392	−0.1481	637.09	636.95
$2\sigma^1 3\sigma^1(^1\Sigma^+)$	−97.0468	−0.0138	−0.0619	0.9913	−0.1150	610.86	610.64
$2\sigma^0(^1\Sigma^+)$	−96.2892	−0.1385	0.1150	0.1178	0.9767	590.24	592.25

calculation for Ne which shows a decrease from 0.951×10^{-3} to 0.701×10^{-3} a.u. for the $2s^2 2p^6(^1S)$ rate.[15] However, the Ne results show an increase from 0.456×10^{-3} to 0.707×10^{-3} a.u. for the $2s^2 2p^4(^1S)$ transition, whereas the transition rate for HF $3\sigma^0(^1\Sigma^+)$ decreases from 0.573×10^{-3} to 0.404×10^{-3} a.u. as a result of configuration mixing. This decrease is partly compensated by an increase in the $1\pi^2(^1\Sigma^+)$ rate such that the net change in the transition rate to these two highest-lying $^1\Sigma^+$ states is very small. Note that the reduction of the $3\sigma^0(^1\Sigma^+)$ rate is due to the interaction with the lower-lying $1\pi^2(^1\Sigma^+)$ state, a feature that is absent in the Ne atom.

The lower symmetry of HF as compared to Ne also allows for mixing of the $^1\Pi$ states and of the $^3\Pi$ states. We have not calculated these mixings explicitly, but expect them to be smaller than for the $^1\Sigma^+$ states, as the Π states do not mix in the atomic case, and the energy separations are quite large. As for Ne, these limited configuration interaction effects will only correspond to a part of the total correlation effect, other contributions expected to be as large or larger.

IV. MIXING OF CONTINUUM ORBITALS BY THE
MOLECULAR FIELD

The spherical waves used for describing the continuum electron in these calculations are not eigenfunctions of the one-electron Hamiltonian carrying the symmetry properties of the molecule [h in Eq. (2)], but of an approximate Hamil-

tonian (h^0). While we consider this a valid approximation in the present case, these continuum orbitals may be improved by using perturbation theory to account for the effect of the neglected part of the Hamiltonian. Taking h' as the perturbation, the first-order correction to the matrix element in Eq. (5) is proportional to

$$\sum_{l'\neq l} \int_{k'=0}^{\infty} dk' \langle \psi_f(k,l)|$$

$$\times \sum_q h'_q|\psi_g(k',l')\rangle(E_A - \tfrac{1}{2}k'^2)^{-1}$$

$$\times \langle \psi_g(k',l')|\sum_{p<r} v_{pr}|\psi_i\rangle, \tag{7}$$

where $\psi_f(k,l)$ is a final state with an outgoing electron of energy $\tfrac{1}{2}k^2$ described by a spherical wave with l quantum number l, and $\psi_g(k',l')$ is an intermediate state with the same electron configuration, but continuum electron described by k'^2 and l'. h'_q is the perturbation operator for the qth electron. We have omitted contributions from bound excited states in Eq. (7), because the interactions are small, and the energy denominators quite large. The matrix element between the final and intermediate states reduces to

$$\langle k,l|h'|k',l'\rangle = \langle k|h_{ll'}(r)(1-\delta_{ll'})|k'\rangle. \tag{8}$$

[δ_{ll} is the Kronecker delta which comes from excluding the case $l=l'$ in the second sum of Eq. (2).] To first order the interaction will therefore only connect continuum functions with $l\neq l'$ in Eq.

TABLE V. Partial and total transition rates for Auger transitions to $^1\Sigma^+$ states in HF with limited CI.

| Final state Main configuration | Partial transition rates (10^{-3} a.u.) | | | Total transition rates (10^{-3} a.u.) | |
	ks	kp	kd	CI	Hartree–Fock
$1\pi^2(^1\Sigma^+)$	0.203	0.000	0.511	0.714	0.594
$3\sigma^0(^1\Sigma^+)$	0.083	0.033	0.288	0.404	0.564
$2\sigma^1 3\sigma^1(^1\Sigma^+)$	0.014	0.506	0.002	0.522	0.642
$2\sigma^0(^1\Sigma^+)$	0.740	0.031	0.000	0.771	0.983

(7). The integral over k' has a singularity at $k' = (2E_A)^{1/2}$, and principal-value integration yields a real and an imaginary contribution. This imaginary part will not contribute to the transition rate in first order of the h' perturbation (lowest-order contribution is real). Calculated values for these imaginary contributions were small, and have therefore been neglected. This leaves a principal-value integration and a sum over l' in Eq. (7).

Our calculations show that the interaction between two continuum orbitals, given by the matrix element in Eq. (8), is small (of order 0.01 a.u.) except for the range $k - 3 < k' < k + 3$ with $k \approx 6.8$ where it may be of the magnitude of 0.5 a.u. This supports the use of h^0 as a first approximation. Corrections to the lowest-order matrix element [Eq. (5)] will only be significant when the correction added by perturbation theory comes from a continuum orbital which itself has an appreciable contribution to the transition rate. We have carried out this perturbation treatment for the following two HF Auger transitions.

A. $1\pi^2(^1\Delta)$

This transition was chosen because it is a dominant feature of the HF Auger spectrum, and because correction to the rate would have to involve the neglected continuum oribtals of l greater than 2. The lowest-order transition rate is due entirely to transitions to the kd continuum orbital, and changes in the total transition rate would have to come from perturbations adding kd contributions to the kf function. The calculations show a first-order correction from Eq. (7) of 0.19×10^{-2} a.u. to the unperturbed kf lowest-order matrix element of 0.03×10^{-2} a.u. The rate for the perturbed kf channel then becomes 0.006×10^{-3} a.u. as compared to 1×10^{-7} before including the kf perturbations. Corresponding mixing of the kf orbital into the unperturbed kd channel leads to a decrease of 0.001×10^{-3} a.u. The total rate for the $1\pi^2(^1\Delta)$ transition is then 1.991×10^{-3} a.u., a negligible change from the spherical-wave result of 1.986×10^{-3} a.u.

B. $3\sigma^0(^1\Sigma^+)$

This transition was chosen because the rate has appreciable contributions from several channels (see Table III). [Other possible candidates are $1\pi^2(^1\Sigma^+)$ and $2\sigma^1 3\sigma^1(^1\Sigma^+)$, neither of which is clearly resolved in the experimental spectrum.] The calculated molecular corrections to the lowest-order matrix element shows how the perturbation affects the transition rate in each partial channel differently (Table VI). For the ks orbital perturbations from the kp and kd channels add 25% to the unperturbed ks Coulomb term resulting in a rate increase of approximately 50%. For the kp orbitals, the corrections come in with opposite sign to the unperturbed matrix element, reducing the rate for this channel by approximately 75%. For the kd orbital, the perturbation corrections are small and of opposite signs. Almost total cancellation therefore leads to only a 1% change in the rate for this partial channel. The net result for the total transition rate to $3\sigma^0(^1\Sigma^+)$ is essentially unchanged.

These two calculations indicate that the use of spherical-wave continuum orbitals as described in Sec. II is a reasonable approximation for Auger transition rates at the Hartree-Fock level in molecules such as HF. The corrections that arise from accounting for a correct molecular potential will be small for transitions that are dominated by one partial channel. For transitions where several partial channels have appreciable rates, there may be significant changes to the rates for individual channels as well as some change to the total rate. Whether there will be cancellation among the correction terms for the separate channels, leaving the total rate largely unaffected as was the case for $3\sigma^0(^1\Sigma^+)$, is not clear. The effect on the total rate may be no greater than the error incurred by neglecting electron correlation.

V. CONCLUSIONS

These calculations show that continuum orbitals

TABLE VI. Lowest-order interaction term [Eq. (5)], first-order molecular corrections, and transition rates for $3\sigma^0(^1\Sigma^+)$ state from perturbation theory.

Main component of perturbed continuum function	Interaction term and first order corrections (a.u.)			Transition rate (10^{-3} a.u.)	
	ks	kp	kd	Perturbed	Unperturbed
ks	0.1071×10^{-1}	0.6160×10^{-3}	0.2012×10^{-2}	0.104	0.067
kp	-0.1036×10^{-2}	0.8301×10^{-2}	-0.3134×10^{-2}	0.009	0.040
kd	0.3252×10^{-3}	-0.9298×10^{-3}	-0.2797×10^{-1}	0.461	0.457

of the spherical-wave type are adequate for describing Auger transition rates at a Hartree-Fock level of accuracy for HF. The same scheme should prove useful in the treatment of other diatomic molecules like OH, HCl, and CH.

For more accurate calculations, better continuum orbitals may be obtained by the use of perturbation theory as discussed in Sec. IV, provided the distortion by the molecular field is not too great for the use of perturbation theory. For calculations accounting also for correlation effects, these improved continuum orbitals should be used. Whether perturbation theory also can provide adequate continuum orbitals for N_2 and CO, depends on the rate of convergence of the pertrubation expansion in Eq. (7). If the sum must be extended to large values of l, this approach may become impractical. It is likely that the approach of this paper will experience considerable difficulties for highly nonspherical systems such as N_2 and CO due to poor convergence properties of the expansion of $1s$ STO. An alternative approach to molecular continuum orbitals has recently been developed by Fliflet and McKoy.[25]

The present calculations emphasize the similarity between Auger processes in HF and the isoelectronic atom Ne at the Hartree-Fock level. At that level, the transition rates are quite closely related. However, a simple CI calculation indicates that correlation effects, although of the same magnitude for the two systems, may be qualitatively different for some transitions. This is due to the greater freedom of interaction afforded by the lower symmetry of the HF molecule.

We have carried out all calculations at a fixed internuclear distance, neglecting bond distortion and vibrational effects. These effects will be increasingly difficult to account for quantitatively as the complexity of the molecules considered increases. Also the single-center approach to continuum orbitals will be difficult to implement in an economical scheme for polyatomic molecules. Still, the techniques used in these calculations should prove useful in the theoretical treatment of Auger transition rates for many diatomic molecules.

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