

Quasimolecular x rays in the Cl^{16+} -Ar collision system

K. Schulze, J. Anton, T. Jacob, W.-D. Sepp, and B. Fricke
Fachbereich Physik, University of Kassel, 34109 Kassel, Germany

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We present molecular-orbital x-ray spectra from collision systems with highly charged projectiles calculated with a time-dependent coupled channel method using relativistic molecular Dirac-Fock-Slater wave functions and full radial and rotational couplings. The spectra of the system Cl^{16+} -Ar are investigated with respect to the dynamics and the number of electrons in the system. Two basis sets have been employed in the calculation, one which belongs to the ground-state configuration and the other to the transition-state configuration on the incoming part of the trajectory respectively. Very good agreement with the experimental results is found by using the transition state basis set.

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I. INTRODUCTION

The investigation of quasimolecular x rays began in 1972 with a publication of Saris *et al.* [1] about noncharacteristic x rays between 0.5–1.5 keV in Ar-Ar collisions. In order to explain the origin of the observed continuous spectra they interpreted the colliding atoms as a diatomic molecule with changing internuclear distance. Already in the sixties, this so-called molecular-orbital model had been applied to interpret results from ion-atom collisions [2,3]. Within this model the electrons in the collision system with velocities greater than the projectile velocity form molecular orbitals (MO's) around the nuclei of projectile and target. Since the internuclear distance changes during the collision the emitted radiation results in a continuous spectrum. After the discovery of the quasimolecular radiation an intensive research in this field¹ followed. There was hope that a tool to perform direct spectroscopy on quasimolecular systems down to the united atom limit had been found. It soon became clear that the spectroscopy by measuring an end point in the spectra is not possible due to the collision broadening [5,6]. Instead of an end point there is an exponential decay of the intensity beyond the transition energy of the united atom [7] which prevents the direct evaluation of the spectra for the measurement of the transition energies.

The theoretical calculations of the spectra which were measured with neutral projectiles required the description of the production of inner shell vacancies which could decay by radiative transitions. Using a gaseous target both processes take place during the same collision in a one-collision process. Using a solid target one can assume the two-collision process where the vacancy is created in a previous collision. Both processes contain serious difficulties for the calculation of the spectra. In the first case one has to describe the ionization of inner shells while in the second case the vacancy is assumed before the collision takes place but the occupation of the remaining levels is not known.

In 1983 a breakthrough was achieved with the application of the acceleration-deceleration method. It allowed the first

impact parameter dependent measurements of the MO x rays emitted in slow collisions of ions bearing a *K*-shell vacancy with a gaseous target (Cl^{16+} -Ar) [8]. Through this development much progress was achieved for the theoretical description. Since the vacancy is brought into the collision in a first approximation the ionization can be neglected and the description of the quasimolecule can be reduced to the inner orbitals. The electronic occupation of the levels at the beginning of the collision is also known. The structure of the spectra is a further important advantage compared to the spectra with neutral projectiles. The coherent superposition of the transition amplitude in the incoming and outgoing part of the trajectory leads to an interference structure which allows a detailed comparison between theory and experiment. However, until 1996 the spectra had only been evaluated using asymptotic integral formulas for the first experimental determination of the $2p\sigma$, $2p\pi-1s\sigma$ transition energies [9–11]. At this time our group published the first *ab initio* calculation of the spectra taking into account radial and rotational couplings [12]. Good qualitative results were found assuming the one-active-electron approximation but also obvious differences between the experimental and the calculated results remained. In this paper calculations in the many-particle framework are presented using two different molecular basis sets. Furthermore, we investigate the influence of the electrons in higher lying orbitals and the dynamic couplings on the intensity and shape of the spectra.

II. METHOD

The semiclassical approximation is applied to describe the system consisting of the two nuclei, the electrons, and the free radiation field. The electrons are treated quantum-mechanically whereas the nuclei move on classical trajectories using the bohr potential.

In the next section we will briefly review the theory of continuum emission during ion-atom collision. It was introduced by Briggs and Dettmann [13] and simplified by Kirsch *et al.* [14] for the many-electron case using field-operator techniques. In Sec. II B we review our method to solve the time-dependent electronic Schrödinger equation and introduce modifications due to an *R*-dependent atomic basis set for the calculation of the molecular basis.

¹A review of this field until 1984 has been given by Anholt [4].

A. Spontaneous photon emission in slow ion-atom collisions

The Hamilton operator of the electron-field system is given through

$$\hat{H} = \hat{H}_e(t) + \hat{H}_{em} + \hat{H}_{int},$$

where $\hat{H}_e(t)$ is the electronic Hamiltonian, \hat{H}_{em} the Hamiltonian of the free radiation field and \hat{H}_{int} the part of the Hamiltonian describing the interaction of the electrons and the radiation field. Since we describe the electrons within the Dirac theory the interaction part of the total Hamiltonian has the form

$$\hat{H}_{int} = e \sum_{j=1}^N \boldsymbol{\alpha}_j \cdot \mathbf{A}(\mathbf{r}_j).$$

The transition amplitude for the transition from the initial atomic state Φ_i to the atomic state Φ_f with a photon $|k, \lambda\rangle$ is given by [13]

$$f_\lambda(t) = \langle \Phi_f(t); \mathbf{k}, \lambda, t | \Psi_{tot}(t) \rangle.$$

$\Psi_{tot}(t)$ is the wave function for the coupled electronic-field system. In first order with respect to the interaction with the radiation field and using the long-wavelength approximation this results in

$$f_{i \rightarrow f \lambda}(t \rightarrow \infty) = -i \left(\frac{2\pi e^2 c^2}{\hbar \omega V} \right)^{1/2} \int_{-\infty}^{\infty} dt e^{i\omega_k t} \times \langle \Psi_f^-(t) | \sum_{j=1}^N \boldsymbol{\alpha}_j \cdot \boldsymbol{\epsilon}_\lambda(\mathbf{k}) | \Psi_i^+(t) \rangle,$$

where $\Psi_f^-(t)$ and $\Psi_i^+(t)$ are solutions of the electronic scattering problem for the boundary conditions $\lim_{t \rightarrow +\infty} \Psi_f^-(t) = \Phi_f(t)$ and $\lim_{t \rightarrow -\infty} \Psi_i^+(t) = \Phi_i(t)$, respectively. $\boldsymbol{\epsilon}_\lambda(\mathbf{k})$ is the polarization vector of the photon and ω_k is the frequency.

Working in the framework of the independent particle model the ansatz for Ψ is given by a Slater determinant. Substituting the ansatz for the electronic wave function in the expression for the transition amplitude one gets [15]

$$f_{i \rightarrow f \lambda}(t \rightarrow \infty) = -i \left(\frac{2\pi e^2 c^2}{\hbar \omega V} \right)^{1/2} \int_{-\infty}^{\infty} dt e^{i\omega_k t} \times \sum_{l,k=1}^N \langle \psi_{f_l}^-(t) | \boldsymbol{\alpha} \cdot \boldsymbol{\epsilon}_\lambda(\mathbf{k}) | \psi_{i_k}^+(t) \rangle S_{fi}(l|k). \quad (1)$$

$S_{fi}(l|k)$ is the minor of the ‘‘nonorthogonal’’ integral of the two Slater determinants

$$S_{fi} = \langle \Psi_f^-(t) | \Psi_i^+(t) \rangle = \det\{s_{fi}(jm)\},$$

where $s_{fi}(jm) = \langle \psi_{f_j}^-(t) | \psi_{i_m}^+(t) \rangle$.

For further investigations we simplify the expression for the transition amplitude (1) by defining the vector

$$\mathbf{D}_{fi}(b, \omega) = \left(\frac{e^2 c^2 2\pi}{\hbar \omega V} \right)^{1/2} \int_{-\infty}^{\infty} dt e^{i\omega_k t} \times \sum_{l,k=1}^N \langle \psi_{f_l}^-(t) | \boldsymbol{\alpha} | \psi_{i_k}^+(t) \rangle S_{fi}(l|k),$$

and by decomposing \mathbf{D}_{fi} into a component parallel to the beam velocity \mathbf{v} , a component parallel to the impact parameter \mathbf{b} and a component perpendicular to the collision plane:

$$\mathbf{D}_{fi} = D_{xfi} \hat{\mathbf{b}} + D_{zfi} \hat{\mathbf{v}} + D_{yfi} \hat{\mathbf{y}}.$$

The emission probability for a photon with the energy E in the solid angle $d\Omega$ by a transition between the electronic states Ψ_i and Ψ_f is now given by

$$\frac{d^2 P}{dE d\Omega}(b, E, \hat{\mathbf{k}}) = \frac{E^2 V}{\hbar^3 c^3 (2\pi)^3} \sum_{\lambda} |f_{i \rightarrow f \lambda}|^2 = \frac{E^2 V}{\hbar^3 c^3 (2\pi)^3} (|\mathbf{D}_{fi}|^2 - |\mathbf{D}_{fi} \cdot \hat{\mathbf{k}}|).$$

The azimuthal angle ϕ is not resolved by the annular photon detector used in the experiment for the system $\text{Cl}^{16+}\text{-Ar}$ [8,11]. We therefore average over the azimuthal angle ϕ and calculate the emission probability in the direction Θ with respect to the beam axis

$$\frac{d^2 P}{dE d\Omega}(b, E, \Theta) = \frac{E^2 V}{\hbar^3 c^3 (2\pi)^3} \left(D_{xfi}^2 + D_{yfi}^2 - \left[\sin^2(\Theta) \left(\frac{1}{2} (D_{xfi}^2 + D_{yfi}^2) - D_{zfi}^2 \right) \right] \right).$$

B. Calculation of the time dependent electronic wave function

The variational principle is employed to find the time-dependent Dirac-Fock (TDDF) equations for the single particle wave functions ψ_l . We substitute the exchange potential in the TDDF equations by the local Slater exchange potential and solve the time dependent Dirac-Fock-Slater (TDDFS) equations

$$\left(c \boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1) m c^2 - \frac{Z_p e^2}{|\mathbf{r} - \mathbf{R}_p(t)|} - \frac{Z_T e^2}{|\mathbf{r} - \mathbf{R}_T(t)|} + e^2 \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \right) \psi_l(\mathbf{r}, t) - 3 X_\alpha e^2 \left(\frac{3}{8\pi} \rho(\mathbf{r}, t) \right)^{1/3} \psi_l(\mathbf{r}, t) = i \hbar \frac{\partial}{\partial t} \psi_l(\mathbf{r}, t) \quad (2)$$

for the one-particle functions $\psi_l(\mathbf{r}, t)$ with $l = 1, \dots, N$ and $X_\alpha = 0.7$. $\mathbf{R}_p(t)$ and $\mathbf{R}_T(t)$ are the coordinate vectors of the projectile and target with respect to the center of mass. $\rho(\mathbf{r}, t)$ is the self-consistent electronic density defined by

$$\rho(\mathbf{r}, t) = \sum_{j=1}^N \psi_j^+(\mathbf{r}, t) \psi_j(\mathbf{r}, t). \quad (3)$$

In this approximation the concept of Slater for a local exchange potential is also used for the time-dependent case and the functions ψ_l are interpreted as approximated solutions of the TDDF equations.

We solve the TDDFS equations (2) by expanding ψ_l in a set of molecular wave functions

$$\psi_l(\mathbf{r}, t) = \sum_{j=1}^M a_{lj}(t) \phi_j(\mathbf{r}, \mathbf{R}(t)) e^{-i(\hbar)^{-1} \int^t \epsilon_j(t') dt'}. \quad (4)$$

The difficulty by solving the TDDFS equations with a basis set expansion is given by the electronic density (3) which cannot be calculated independent of the collision process. Therefore the molecular basis set—in terms of which the collision process is to be analyzed—is dependent on the collision process itself. In our group there has been an attempt to solve this problem in terms of a time-window-method [16] but this procedure is not appropriate for the calculation of MO x rays. For this reason we chose a different approach [17] which shall be described in the following.

The molecular wave functions $\phi_j(\mathbf{r}, \mathbf{R})$ are chosen as solutions of the stationary Dirac-Fock-Slater equations which are solved using the LCAO-MO method [18]. The main focus of developing another approach was first to obtain accurate molecular wave functions and energy eigenvalues over the whole range of internuclear distances. Secondly we were concentrating on the question of the distribution of the electrons during the collision approximately without losing accuracy. For these reasons we have developed an “atomic” basis set for the diagonalization of the molecular Hamiltonian which is dependent on the internuclear distance R . The basis set results from three atomic Dirac-Fock-Slater calculations [17]. The wave functions included are located at the two atomic centers and at the center of charge, respectively. For the calculation of the wave functions at the center of charge the external potential is given by the monopole part of the two-center potential. Calculating the basis functions at the target and projectile, respectively, the monopole part of the second nuclei is taken into account. In summary the external potentials in the atomic DFS equations are replaced by

$$V_T(r_T) \rightarrow V_T(r_T) + V_P^0(r_T, R), \quad (5)$$

$$V_P(r_P) \rightarrow V_P(r_P) + V_T^0(r_P, R), \quad (6)$$

$$V_M(r_C) \rightarrow V_P^0(r_C, R_P^C) + V_T^0(r_C, R_T^C). \quad (7)$$

r_T corresponds to the distance of the electron with respect to the nuclei of the target. r_P and r_C correspond to the distance with respect to the nuclei of the projectile and the center of charge, respectively. $V_P^0(r_T, R)$ is the monopole part of the potential of the projectile nuclei with respect to the target nuclei at the distance R from the projectile. Accordingly defined are $V_T^0(r_P, R)$, $V_P^0(r_C, R_P)$ and $V_T^0(r_C, R_T)$, where R_P^C

and R_T^C are the distances of the projectile and the target nuclei from the center of charge.

Furthermore we extend the external potentials given by Eqs. (5)–(7) for the monopole part of the coulomb and exchange potentials of the electrons in the other two centers. For doing so we use the division of the molecular electronic density at the preceding internuclear distance in three spherical parts with the Mulliken population analysis [19] of the basis functions. The electrons correlating with the calculated set are taken into account self-consistently.

The solution of the atomic DFS equations is based on the program RADWEQ by Salvat and Mayol [20] for the solution of the Schrödinger or Dirac equation for central fields. With this method we achieve a very accurate solution of the molecular DFS equations for all internuclear distances [17]. This is necessary for the calculation of the molecular x-ray spectra since the behavior at large internuclear distances as well as the united atom behavior has to be described. Furthermore this method allows accurate transition state calculations which enables one to model the electronic density during the collision approximately.

Insertion of the expansion (4) in the TDDFS equations (2) with the electronic density (3) approximated by the molecular electronic density leads to the coupled channel equations

$$i\hbar \dot{a}_{lj}(t) = \sum_{k=1}^M a_{lk}(t) \langle \phi_j(t) | -i\hbar \frac{\partial}{\partial t} | \phi_k(t) \rangle, \quad l = 1, \dots, N \quad (8)$$

for the occupation amplitudes $a_{lj}(t)$.

The numerical evaluation of the dynamic coupling matrix elements

$$\langle \phi_j | \frac{\partial}{\partial t} | \phi_k \rangle = \langle \phi_j | \dot{R} \frac{\partial}{\partial R} | \phi_k \rangle + \langle \phi_j | \dot{\Theta} \frac{\partial}{\partial \Theta} | \phi_k \rangle$$

has been described in detail elsewhere [21]. This evaluation has to be extended due to the explicit R -dependence of the atomic basis set. An additional term which results from

$$\begin{aligned} \frac{\partial}{\partial R} \chi_l(\xi_Z(\mathbf{r}, \mathbf{R}), R) &= -\frac{i}{\hbar} C_Z p_z \chi_l(\xi_Z(\mathbf{r}, \mathbf{R}), R) \\ &+ \frac{\partial}{\partial R} |_{\xi_Z} \chi_l(\xi_Z(\mathbf{r}, \mathbf{R}), R) \end{aligned} \quad (9)$$

has to be added to the displacement part of the radial coupling matrix element [21]. Here C_Z with $Z=T, P$ and C is given by

$$C_{T,P} = \frac{(\pm)M_{P/T}}{M_T + M_P}, \quad C_C = \frac{Z_T C_T + Z_P C_P}{Z_P + Z_T},$$

respectively, and $\xi_Z(\mathbf{r}, \mathbf{R}) = \mathbf{r} - \mathbf{R}_Z$. The second term in Eq. (9) results from the changing external potential used for the construction of the basis functions. This term is calculated by solving the atomic DFS equations for two neighboring internuclear distances with the corresponding external potentials but with the same occupation numbers of the orbitals.

With the expansion (4) of the time-dependent wave function ψ_{ii}^+ and ψ_{kl}^- the transition amplitude $f_{i \rightarrow f\lambda}$ (1) takes the form

$$\begin{aligned} f_{i \rightarrow f\lambda}(t \rightarrow \infty) &= -i \left(\frac{2\pi e^2 c^2}{\hbar \omega V} \right)^{1/2} \int_{-\infty}^{\infty} dt \left\{ e^{i\omega t} \sum_{l,k=1}^N S_{fi}(l|k) \right. \\ &\quad \times \left(\sum_{j,m=1}^M a_{fij}^- * a_{ikm}^+ \langle \phi_j(t) | \boldsymbol{\alpha} \cdot \boldsymbol{\epsilon}_\lambda(\mathbf{k}) \right. \\ &\quad \left. \left. \times | \phi_m(t) \rangle e^{-i(i/\hbar) \int_{-\infty}^t dt' (\epsilon_m - \epsilon_j)} \right) \right\} \\ &= -i \boldsymbol{\epsilon}_\lambda(\mathbf{k}) \cdot \mathbf{D}_{fi}(\mathbf{b}, E_i, \omega), \end{aligned} \quad (10)$$

where $a_{ikm}^+(t)$ and $a_{fij}^-(t)$ are solutions of the coupled channel equations (8) for the boundary conditions $a_{fij}^-(t \rightarrow \infty) = \delta_{fij}$ and $a_{ikm}^+(t \rightarrow -\infty) = \delta_{ikm}$, respectively.

The transition amplitude is evaluated in the center of mass system which makes it necessary to transform the molecular dipole matrix elements. If the vector $\mathbf{R}(t)$ connecting the two nuclei forms the angle $\Theta(t)$ with the z -axis of the center of mass system the transformation is given by $\boldsymbol{\alpha}_{jm} = D(t) \boldsymbol{\alpha}'_{jm}$ with

$$D(t) = \begin{pmatrix} \cos \Theta(t) & 0 & \sin \Theta(t) \\ 0 & 1 & 0 \\ -\sin \Theta(t) & 0 & \cos \Theta(t) \end{pmatrix}. \quad (11)$$

Usually the final state of the electronic system is not detected so that the transition amplitude has to be calculated for all possible final states. The evaluation of the intensity $I = \sum_f |f_{i \rightarrow f\lambda}|$ is simplified by replacing the $(-)$ -states with future boundary conditions by $(+)$ -states which is a method introduced by Kirsch *et al.* [14]. The advantage of this method is the possibility to evaluate $S_{fi}(l|k)$ in Eq. (10) directly since it is given by a Kronecker delta in this case.

III. RESULTS

The system $\text{Cl}^{16+}\text{-Ar}$ was the first system being investigated with the acceleration-deceleration method [8]. Measurements exist for different impact energies as well as for varying impact parameters [11]. Therefore it is an excellent system for the analysis of the theoretical approximations. We improve here our previous calculation on the collision system $\text{Cl}^{16+}\text{-Ar}$ [12]. For low impact energies the intensity is overestimated and the oscillatory structure in the experimental data smeared out compared with the structure of the calculated spectra where the intensity at the minima is nearly zero. Furthermore the structure of the calculated spectra is slightly shifted to lower energies. It was assumed that one reason for this was the one-active-electron approximation. In this paper we are presenting results calculated in the many-particle framework with different numbers of electrons in the system. We investigate the dependence of the spectra on the adiabatic density approximation by using two basis sets with

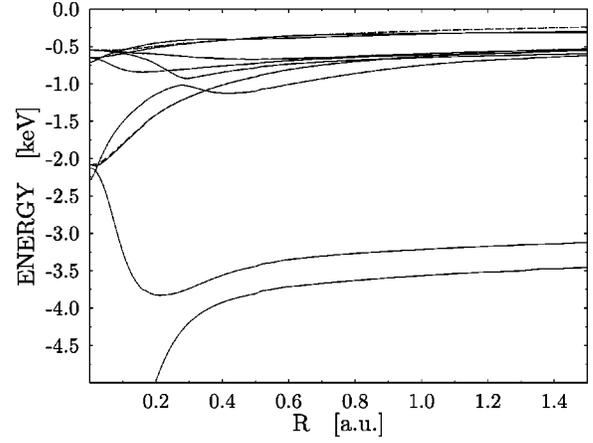


FIG. 1. Correlation diagram for the system $(\text{ClAr})^{16+}$ in the ground state. Presented are the levels corresponding to the K , L , and M shell of the united system.

occupations of the molecular orbitals corresponding to the borderline cases and the dependence on the dynamics.

A. Energy eigenvalues from two different molecular basis sets

In the adiabatic approximation for the electronic density the difference between the time dependent electronic density and the molecular electronic density is neglected which results in the coupled channel equations (8). Up to now we always had calculated molecular basis sets in the ground state [12,22] for the calculation of the MO x-ray spectra. In the present work we present a second basis set which corresponds to the state in the incoming part of the trajectory. With these two basis sets we can represent the two limiting cases of the occupation of the molecular orbitals during the collision. While all electrons are assumed to de-excite immediately in the ground state, in the new basis set the occupation does not change during the collision process. Due to numerical difficulties the electrons in the M -shell of Ar are neglected in this calculation. To prevent strong charge exchange at narrow crossings the occupation is continued diabatically.

In Fig. 1 and 2 parts of the two correlation diagrams are presented. Both calculations have been started at $R=4$ a.u. with a basis set consisting of the $1s_{1/2}\text{-}3p_{3/2}$ orbitals of Cl^{16+} and Ar (Ar^{8+}) and the $1s_{1/2}\text{-}4d_{7/2}$ monopole functions at the center of charge. For decreasing internuclear distances the ‘‘atomic’’ basis functions for the diagonalization of the molecular Hamiltonian are modified as described in Sec. II B. (Due to the different molecular occupation numbers the results of the Mulliken population analysis are different in the two cases.)

A principal difference in the behavior of the molecular one-particle energies is seen for the two strongest bound levels. While the levels in the ground state configuration are almost parallel till $R \sim 0.4$ a.u., there is a narrow crossing at $R \sim 0.73$ a.u. in the transition state calculation. In the latter the energetical position is reproduced correctly. Due to the high degree of ionization of the chlorine atom the energetical position of the $1s_{1/2}$ levels is exchanged. The effect which

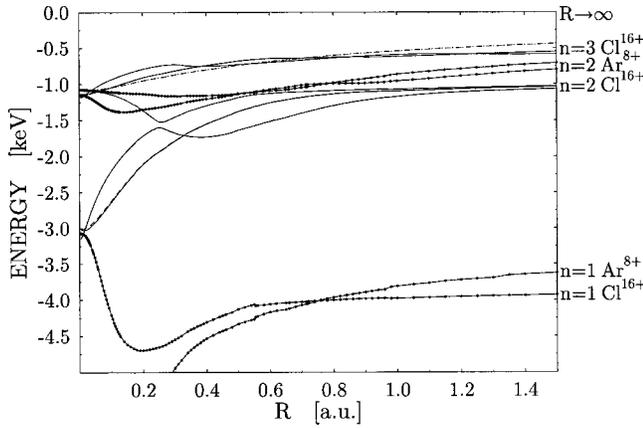


FIG. 2. Correlation diagram for the system $(\text{ClAr})^{24+}$ with a transition state occupation which corresponds to the asymptotic occupation of the collision partners (see text). Presented are the levels corresponding to the K , L , and M shell of the united system. The occupied levels are additionally marked with dots at the calculated internuclear distance.

leads to the approach of the two levels is the weakly screened nuclear potential of the chlorine. In the ground state calculation the electrons are distributed equally among both atoms so that the strongest bound level belongs to argon for all internuclear distances.

A similar behavior is found for the levels which correspond to the L -shells of the collision partners: For the molecular transition state basis the atomic level structure is still seen until $R=1.5$ a.u., but at this distance the L -shell of argon is already energetically lower than the M -shell of chlorine due to the chlorine nuclei. A purely atomic behavior at this distance is not found but the leading terms in the expansion of the molecular orbitals still allow to make a definite characterization of the orbitals. In the ground state calculation the sequence of the levels is different. The $2s$ levels of the collision partners are followed by the $2p$ levels of Ar and than the $2p$ levels of Cl. Here the difficulties using a molecular basis set from ground state calculations become obvious. The definition of the boundary conditions for the solution of the coupled channel equations (8) can neither be given using the energetical order of the levels nor using the leading terms in the molecular expansion. For this reason the results of the transition state calculation are used for the definition of the boundary conditions for the ground state as well.

For $R < 0.4$ a.u. the structure in the correlation diagram belonging to the transition state calculation is shifted to smaller internuclear distances but there are no principal deviations from the ground state calculation. A distinct difference is found in the energetical position of the one-particle energies due to the varying electronic screening. Decisive for the solution of the coupled channel equations (8) and the calculation of the transition amplitude (10) are the transition energies which are plotted in Fig. 3 for the transitions between the $1s_{1/2}\sigma$ level and the $2p_{1/2}\sigma$, $2p_{3/2}\pi$, $3p_{1/2}\sigma$ and the $3p_{3/2}\pi$ levels. The differences of the energy eigenvalues from the ground state calculations are systematically smaller than the corresponding values resulting from the transition

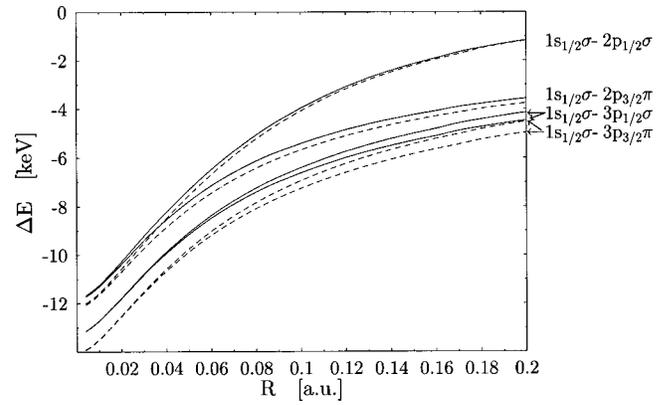


FIG. 3. Differences of the molecular one-particle energies between the ground state calculations (solid lines) and the transition state calculations (dashed lines) as function of the internuclear distance R . Compared are the energy differences between the $1s_{1/2}\sigma$ level and the $2p_{1/2}\sigma$, $2p_{3/2}\pi$, $3p_{1/2}\sigma$, and the $3p_{3/2}\pi$ levels, respectively. The characterization of the molecular levels is done with the notation in the limit of the united atom.

state calculations. A quantitative analysis of the effect for the spectra cannot be performed on this level but the spectra calculated with the transition state basis set will be shifted to higher energies.

B. Molecular x-ray spectra—the dependence on the electron distribution

In a previous paper [12] we have presented quasimolecular x-ray spectra which were calculated in the one-active electron approximation. The dependence of the structure on the impact energy and the impact parameter could be reproduced but the remaining differences from the experimental data requires further investigations.

In the calculation of the transition amplitude the electron distribution enters twofold due to the adiabatic approximation of the electronic density: In the time dependent wavefunction Ψ_i^+ which is defined through the boundary conditions at $t \rightarrow -\infty$ and with the static molecular electronic density in the energy eigenvalues and matrix elements. Here both dependences shall be investigated.

In the one-electron approximation Ψ_i^+ and Ψ_f^- are not represented by Slater determinants but by one-particle wave functions. Out of the 10 molecular orbitals (K and L shell of the united atom) which have been taken into account in the one-electron calculations [12] asymptotically the $1s_{1/2}\sigma$ is fully occupied and the $2p_{1/2}\sigma$ level is occupied with one electron. The remaining orbitals correspond to the L -shell of Cl^{16+} for $R \rightarrow \infty$ and are therefore empty. Firstly we want to report on calculations which are performed within the subspace spanned by the same 10 molecular orbitals but which take into account the right occupation within this basis set. We find that the structure of the spectra is identical to the one found in the one-electron approximation [12] but now the intensity lies within the systematic error given by the experimentalists [11]. In the one-electron approximation the intensity was overestimated by a factor of 2.2 for an impact energy of 20 MeV, a factor of 5.5 for 5 MeV [12] and 9.0 for

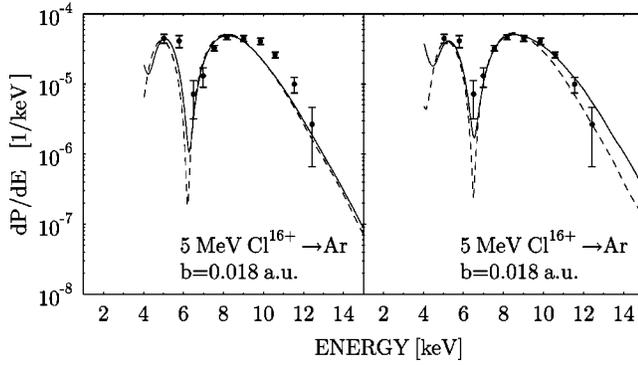


FIG. 4. Investigation of the emission probability of a photon 90° with respect to the beam axis in collisions of 5 MeV Cl^{16+} on Ar with respect to the electron distribution (see text). The impact parameter is $b=0.018 \text{ a.u.}$ The spectra in the left representation result from calculations with molecular basis functions from ground state calculations, while the calculations of the spectra in the right picture are based on transition state calculations. In both pictures calculations are compared which differ in the number of the molecular basis functions as well as in the number of the electrons which are taken into account. While one calculation is based on nine electrons in a basis set of 28 molecular orbitals (K , L , and M shell of the united system) (solid line), the results of the second calculation are achieved in a subspace of 10 basis functions (K and L shell of the united atom) with the three electrons contained therein (dashed line). The experimental data are taken from [11]. Experimental and theoretical values are multiplied with 4π . See text for the normalization.

2.5 MeV. In the many-particle framework the intensity is scaled with a factor of 0.8 for 20 MeV and 0.59 for 5 MeV and 2.5 MeV and therefore lies within the scope of the error given by the experimentalists (intensity can be low by as much as a factor 3). With these results the deviation in the absolute height of the intensity which could not be explained before [12] can be traced back to the one-active-electron approximation.

The inclusion of further electrons leads to a reduced intensity due to the initially non-existing vacancy in the $1s_{1/2}\sigma$ orbital. It may also lead to additional contributions in the transition amplitude. In the following we investigate the effect of the electrons in higher lying orbitals on the structure of the MO x rays. The basis set is extended to 28 molecular orbitals which correspond to the K , L , and M shell of the united system. Six of the additional levels are initially occupied since they originate from the $n=2$ shell of argon. One result of the calculations is presented in Fig. 4 on the left side in comparison with the three-electron calculation described above. (The principal differences do not depend on the impact energy and impact parameter.) For comparison the results of the new calculations are scaled to the same intensity with a factor of 0.35. One can see that the contributions of the additional electrons lead to a structure which is smeared out at the minimum. With respect to the structure at the minimum the inclusion of the additional electrons leads to an improved result but not to a better agreement with the experimental result for high photon energies which was assumed before [12].

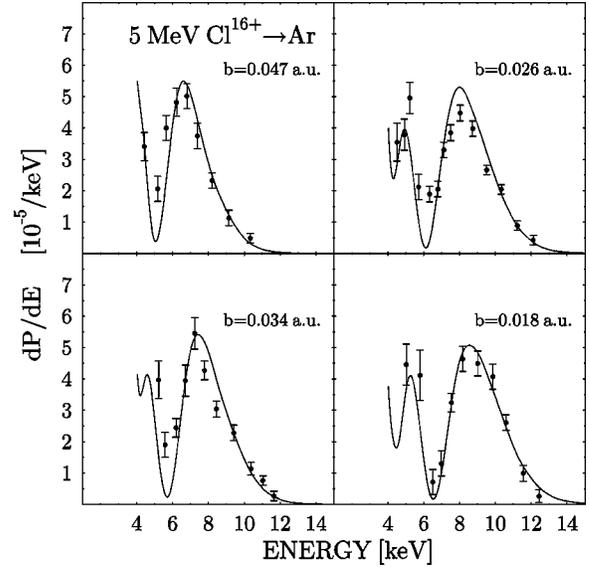


FIG. 5. Emission probability of a photon 90° with respect to the beam axis in collisions of 5 MeV Cl^{16+} on Ar for different impact parameters. In the calculations the orbitals corresponding to the K , L , and M shell and the nine electrons contained therein have been taken into account. The molecular basis functions result from transition state calculations with the asymptotic occupation of the orbitals (Sec. III 1). Experimental results are taken from [11]. Experimental and theoretical values are multiplied with 4π . See text for the normalization.

It is justified to assume that the remaining differences are due to the static molecular electronic density. To investigate the effect of the molecular occupation numbers on the spectra the same calculations are performed with the transition state basis set described in the previous section. The effect will be analyzed by comparison of the left and the right picture in Fig. 4. The spectra on the right result from calculations using the transition state basis set. The scaling constants are 0.41 for the three-electron calculation and 0.33 for the nine-electron calculation. With the application of the transition state basis set the intensity for the three-electron calculation is increased which could be expected due to bigger dipole matrix elements. Furthermore the minima and maxima are shifted to higher photon energies which leads to a better agreement with the experimental results. Obviously the excited molecule describes the collision system $\text{Cl}^{16+}\text{-Ar}$ better than the molecule $(\text{ClAr})^{16+}$ in the ground state.

In Fig. 5 the emission probability of a photon in collisions of Cl^{16+} on Ar calculated using the transition state basis set and including nine electrons is compared with the experimental results of Schuch *et al.* [11] for different impact parameters and an impact energy of 5 MeV. The structure is very well compatible with the experimental results and the intensity lies within the systematic experimental error.

C. Spectra without the inclusion of dynamic coupling

The interference structure in the spectra which results from the coherent superposition of the transition amplitudes on the incoming and outgoing parts of the trajectory has been evaluated using asymptotic integral formulas [23]. This leads

to the first experimental determination of MO transition energies as a function of the internuclear distance [9–11]. The asymptotic integral formulas are applied to evaluate the transition amplitude within the theory of collision broadening of Weisskopf [5]. This theory takes into account the time dependence of the molecular dipole matrix elements and the transition energies but does not consider the time-dependent occupation amplitudes due to the dynamic coupling of the molecular orbitals. Therefore the ansatz for the time-dependent electronic wave function is given by

$$\psi_k(t) = \phi_k(\mathbf{r}, \mathbf{R}(t)) e^{-(i/\hbar) \int_{-\infty}^t \epsilon_k(t') dt'}$$

With this ansatz the transition amplitude in the one-electron approximation is reduced to the Fourier transform of the time-dependent molecular dipole matrix element

$$f_{i \rightarrow f \lambda}(t \rightarrow \infty) = -i \left(\frac{2\pi e^2 c^2}{\hbar \omega V} \right)^{1/2} \boldsymbol{\epsilon}_\lambda(\mathbf{k}) \int_{-\infty}^{\infty} dt e^{i\omega_k t} \times \underbrace{d_{if}(\mathbf{R}(t))}_{\langle \phi_f(t) | \boldsymbol{\alpha} | \phi_i(t) \rangle} e^{-(i/\hbar) \int_{-\infty}^t \epsilon'_m dt' (\epsilon_m - \epsilon_j)}. \quad (12)$$

In the following this approximation is analyzed by the numerical evaluation of Eq. (12) for the transitions $2p_{1/2}\sigma$, $2p_{3/2}\pi-1s_{1/2}\sigma$. Before the results will be presented we shall discuss whether these transitions can contribute to the intensity. In the discussion about their results Schuch *et al.* [11] mentioned that the contribution from the $2p\pi$ level should be dominant due to the larger number of electrons. In the discussion about the molecular basis set in Sec. III 1 it could be seen (Fig. 2) that within the K and L shell of the united atom only the $1s_{1/2}\sigma$ is fully occupied and the $2p_{1/2}\sigma$ level is only occupied with one electron. Therefore the transition $2p\pi-1s\sigma$ can only contribute to the intensity through the dynamic population of the $2p\pi$ level during the collision. For this reason the calculations of Eq. (12) for this transition cannot be motivated by the asymptotic occupation but can only serve for the analysis.

On the left side in Fig. 6 the results for the relevant transition are compared with the one-electron calculation [12] and the experimental results [11]. All calculations are performed using the ground state basis set and the intensities are scaled with the same constant (Sec. III B). It is seen that the structure deviates strongly from the experimental results and the dynamic calculation. The fact that the results for the transition energies evaluated with the stationary phase approximation and the uniform asymptotic approximation [9,11,23] are in good agreement with DFS calculations [24] has nevertheless the following reason: In the evaluation of the experimentalists the rotation of the internuclear axis (11) is neglected. Because of the transformation with Eq. (11) $d_{if}(\mathbf{R}(t))$ is not a gerade function of t which was assumed by the experimentalists [9,11] (see also [13]). Neglecting the transformation in the calculations results in spectra presented on the right side in Fig. 6 which agree quite well with the experimental results.

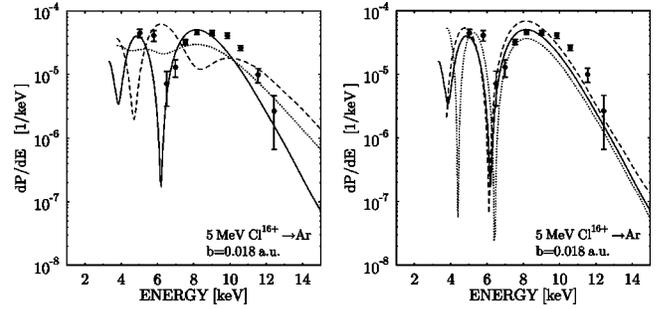


FIG. 6. Analysis of the emission probability of a photon 90° with respect to the beam axis in collisions of 5 MeV Cl^{16+} on Ar as function of the photon energy in different approximations. The impact parameter is $b=0.018 \text{ a.u.}$ Left side: Calculations in the one-electron approximation (solid line) [12] are compared with spectra through the transitions (constant occupation of the orbital during the collision) $2p_{3/2}\pi-1s_{1/2}\sigma$ (dotted line) and $2p_{1/2}\sigma-1s_{1/2}\sigma$ (dashed line). Right side: Similar to the left side, but in these calculations the transformation of the dipole matrix elements (11) is neglected additionally. Experimental data are taken from [11].

These results confirm the statement of Anholt [25] that the rotational coupling prevents the rotation of the $2p\sigma$, $2p\pi-1s\sigma$ dipoles with the internuclear axis for collisions with small impact parameter. Only because of this effect it can be assumed that $d_{if}(\mathbf{R}(t))$ is a gerade function for the evaluation of the spectra.

IV. CONCLUSION

We were motivated by the possibility of investigating the inner states in superheavy quasimolecules with energy eigenvalues in the vicinity of the negative continuum. We have calculated the emission probability of photons in ion-atom collisions with hydrogenlike and fully ionized projectiles and analyzed the dependence of the spectra on the theoretical approximations.

The calculation of the time-dependent electronic wave function in the independent particle model was performed by the solution of the time-dependent DFS equations in the adiabatic density approximation. For the investigated system $\text{Cl}^{16+}\text{-Ar}$ it was not to be expected that molecular ground state calculations would give an optimal approximation of the time-dependent density.

For the investigation of the dependence of the MO x-ray spectra on the adiabatic density used for the calculation of the time-dependent wave function we have calculated the photon emission probability in collisions of Cl^{16+} on Ar with two different basis sets. They resulted from molecular DFS calculations with a different occupation of the molecular orbitals. In the calculation of the first basis set the occupation corresponded to the molecule $(\text{ClAr})^{16+}$ in the ground state (ground state calculation). The second basis set has been calculated with the asymptotic occupation of the orbitals in the incoming part of the trajectory (transition state calculation). Furthermore, we have analyzed the influence of transitions from higher levels on the spectra. The calculated spectra could be tested in comparison with experimental data [11]. The following results were achieved.

The asymptotic correlation of the molecular states achieved from ground state calculations with the collision partners is necessary for the choice of the boundary conditions. It cannot be performed without additional informations. The correlation can be found without any difficulties by using the transition state basis set.

With the molecular basis set resulting from transition state calculations very good agreement of the calculated results with the experimental data is achieved. Using the ground state calculations the calculated spectra are shifted to smaller photon energies compared to the experimental results. The shift of the structure between the two calculations amounts to ≈ 0.3 keV. The transition state basis set leads to an improved agreement with the experimental results since the density in the collision system can be approximately described.

The structure of the experimental spectra is smeared out. In our investigations this behavior is due to the dynamics as well as the contributions of electrons in the L shell of argon.

The absolute intensity taken from our calculations where the electrons in the K and L shell of argon contribute lies within the experimental systematic error. Use of the transition state basis set leads to an intensity which is found to be

little higher compared to the ground state calculations. This can be explained by the greater matrix elements for small internuclear distances due to less screening.

With these results it is shown that the investigation of quasimolecular radiation in collisions with hydrogenlike projectiles is very suitable for the investigation of the energy eigenvalues of the quasimolecule as well as the dynamic behavior during the collision. But the advantages for the theoretical description—first only a small number of inner states of the quasimolecule have to be taken into account and secondly the initial occupations are defined—are opposed by the difficulty to calculate the highly excited system. The principal structure of the spectra can be calculated with the usage of ground state basis sets but for a test of the energy eigenvalues in the vicinity of the negative continuum the excitation should be taken into account. This can be done approximately by using transition state calculations.

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