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$2p_\pi - 2p_\sigma$ Crossing in Heavy Symmetric Ion-Atom Collisions

I. Level Structure *

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Ab initio self-consistent DFS calculations are performed for five different symmetric atomic systems from Ar-Ar to Pb-Pb. The level structure for the $2p_\pi - 2p_\sigma$ crossing as function of the united atomic charge Z_u is studied and interpreted. Manybody effects, spin-orbit splitting, direct relativistic effects as well as indirect relativistic effects are differently important for different Z_u. For the I-I system a comparison with other calculations is given.

I. Introduction

Briggs and Macek [1] recognized the dominant role of the $2p_\pi - 2p_\sigma$ rotational coupling for the K-shell vacancy production during heavy ion collisions. Later a scaling law for the excitation probability due to this coupling was proposed [2–4]. The excitation probability is usually obtained in the semi-classical approximation by integration of the coupled differential equations for the complex amplitudes along a prescribed colliding trajectory $R(t)$ between the two nuclei. Unfortunately, the scaling law yields reasonable results only for the light systems with nuclear charges $Z_1, Z_2 \lesssim 20$. For heavier systems, many body effects, spin-orbit splitting and other relativistic effects, which will be discussed in part IV, lead to discrepancies with the assumed energy difference in the scaling law of $\Delta E(R) \sim R^2$ between the $2p_\pi$ and $2p_\sigma$ levels at small internuclear distances. In addition the change in the wavefunctions due to the relativistic parts of the Hamiltonian will change the behaviour of the scaled coupling matrix elements which then also will affect the excitation probability. To explain the observed differences in heavy systems two new attempts [5–6] were made to establish a new scaling law for relativistic systems but again they do not compare well with experiment [6, 7].

We try to investigate these discrepancies in two steps. In this paper we calculate good correlation diagrams using a sophisticated Dirac-Fock-Slater (DFS) code which successfully has been applied to numerous systems [8]. In part II of this paper we briefly discuss the method of calculation. In part III we compare the non-relativistic and relativistic structure of the $2p_\pi - 2p_\sigma$ coupling region. In part IV we present the results of ab initio calculations for five symmetric colliding systems from Ar-Ar, Kr-Kr, I-I, Yb-Yb up to Pb-Pb and discuss the changing behaviour for the various levels. In part V we compare the level structure for the I-I system from four different calculations. Because ab initio coupling matrix elements of the same order of sophistication are not yet available we present in a forthcoming second paper good matrix elements and use them together with the information from this paper in coupled channel calculations in order to see the changing structure of the transition probabilities $P(b)$ as function of impact parameter which originates from the changes of the level structure and wavefunctions for the higher Z systems. This detailed investigation is necessary because the K-vacancy production probabilities in heavy collision systems is still not well understood.

II. Method of Calculation

The calculations can be described briefly as follows [9]. The relativistic one-electron Hamiltonian is given by

$$h = \alpha c \cdot p + \beta m c^2 + V(r),$$

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where $c\alpha \cdot p + \beta m c^2$ are the kinetic and rest energy operators. $V(r)$ is the potential energy operator which can be divided as usual into the Coulomb and exchange terms. This last part is obtained from the molecular charge density using the Slater $X\alpha$-method with the exchange parameter $\alpha = 0.70$. A variational method is used to find the molecular wavefunctions, which are approximated by a linear combination of symmetry orbitals constructed from atomic numerical basis functions. The basis set for the atoms have been generated in the ground state configuration of the degree of ionization shown in Fig. 2a to 2e. A large extended basis set is used in all cases. The basis states were prediagonalized to avoid linear dependencies at small internuclear distances. The Dirac-Fock-Slater and overlap matrix elements were evaluated by using the discrete variational method as described in earlier calculations [10]. The molecular potential was determined in the successive iterations from Mulliken gross orbital populations for the basis functions. These populations were spherically averaged and the molecular potential was constructed from the spherical charges on the constituant atoms. Self-consistency was obtained when the input and output orbital charges were equal. This procedure does not imply spherical symmetry of the molecular potential as for example in the "muffin-tin" form used in the multiple scattering method (MS $X\alpha$) [11].

III. Comparison of the Non-Relativistic and Relativistic Structure of the $2p_\pi - 2p_\sigma$ Coupling

Due to the spin-orbit coupling every non-relativistic level with an angular momentum $l > 0$ splits into two sublevels with a total angular momentum $j_+ = l + \frac{1}{2}$ and $j_- = l - \frac{1}{2}$. Since in diatomic molecules the projection of the total angular momentum on the internuclear axis m_j is the only good quantum number we get in the relativistic case only levels with maximal 2 electrons. Thus a non-relativistic σ-level with $m_l = 0$ is described in the relativistic case by $m_j = \pm 1/2$ and is therefore called a (1/2)-level. The π-level with $m_l = \pm 1$ which carries 4 electrons splits in the relativistic case into two sublevels with $m_j = \pm 3/2$ which is called a (3/2)-level and $m_j = \pm 1/2$ which again is a (1/2)-level. In addition, for the homonuclear case parity is also a good quantum number.

In Fig. 1 we compare the general behaviour of the levels for the homonuclear and heteronuclear case in the non-relativistic and relativistic description. In the homonuclear non-relativistic description only the $2p_\pi - 2p_\sigma$ rotational coupling is effective. Since

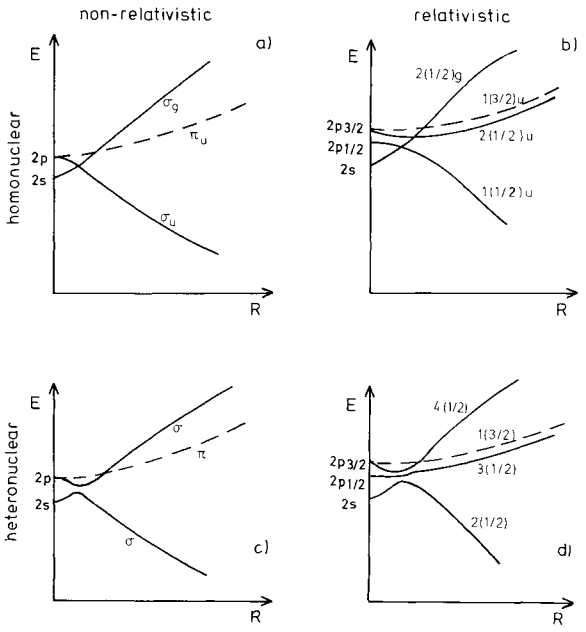

Fig. 1. Schematic adiabatic level structure in the vincinity of the $n = 2$ united levels for non-relativistic and relativistic description and homonuclear and heteronuclear cases

neither rotational nor radial coupling contain parity changing operators, the $2s_\sigma$-level is decoupled from the other levels in Fig. 1a. The $2p_\pi$ and $2p_\sigma$ levels degenerate at $R = 0$ and their energy splitting $\Delta E(R)$ for small Z-systems is more or less $\sim R^2$ for small internuclear distances. This structure and behaviour is the basis of the scaling law for the $2p_\pi - 2p_\sigma$ rotational coupling [2-4].

The relativistic description is shown in Fig. 1b; several differences are apparent. First, the level corresponding to the non-relativistic $2p$-united level splits into two levels: $2p_{1/2}$ and $2p_{3/2}$. Second, in a quasimolecule the relativistic $2p_{3/2}$-level splits into a $(3/2)_u$- and $(1/2)_u$-level both together corresponding to the $1\pi_u$-level in the non-relativistic case. This leads to several complications. Adiabatically the $1(1/2)_u$-level which in the non-relativistic description is the $2p_\sigma$-level now corresponds to the $2p_{1/2}$-united level for $R = 0$ but diabatically proceeds to the $2p_{3/2}$-united level the same level where the $1(3/2)_u$-level ends up. Due to the molecular field the $1(3/2)_u$- and $2(1/2)_u$-levels are non-degenerate in the molecule. As a result one finds two rotational couplings between the $1(3/2)_u$-level and the two $(1/2)_u$-levels. In addition we have one radial coupling at $R \neq 0$ between the two $(1/2)_u$-levels. In general this radial coupling for small Z-systems is expected to be zero so that in the limit of small Z this directly converges into the non-relativistic description of Fig. 1a.

Fig. 1c and d show the same level structure for the heteronuclear case where parity is no good quantum

number any more. In the non-relativistic case this leads to two rotational couplings and one radial coupling whereas in the relativistic description one already gets three rotational and two radial couplings.

IV. Discussion of the Level Structure for Heavy Z-Systems

To get an idea of how the level structure of the discussed crossings look like in real systems we performed five ab initio calculations over the whole region of possible Z-systems. Figure 2 shows the results for the symmetric systems Ar-Ar ($Z_u=36$), Kr-Kr ($Z_u=72$), I-I ($Z_u=106$), Yb-Yb ($Z_u=140$), and Pb-Pb ($Z_u=164$) in a scaled procedure. The abscissa are given in units of $\frac{2a_0}{Z_u}$ and the ordinates are scaled in $\frac{\text{eV}}{Z_u^2}$. (For the sake of clearness the $2(1/2)_g$-level is left out.) The system Ar-Ar is still very much comparable to the non-relativistic small Z case. The spin-orbit splitting is small thus strong radial coupling between the $(1/2)_u$-level occurs. An interesting detail is that the $2(1/2)_u$- and $1(3/2)_u$-levels for larger distances have an energy which fits better the $2p_{1/2}$-united level rather than the $2p_{3/2}$-level. In the case of Kr-Kr the spin-orbit splitting has increased, the radial coupling between the two $(1/2)_u$-levels is fully developed. The splitting between the $1(3/2)_u$- and $2(1/2)_u$-levels starts to be significant for medium internuclear distances where the molecular splitting becomes important. When the internuclear distance becomes so large that the two $n=2$ atomic wavefunctions are well separated the $1(3/2)_u$- and the $2(1/2)_u$-levels have to become degenerate again according to their atomic character in the separated atom limit. As can be seen in Fig. 2 this criterium is fulfilled in our calculations.

For the I-I system with $Z_u=106$ the spin-orbit splitting already amounts to 30% of the binding energy of the $2p_{3/2}$-level. This pushes the radial coupling to larger internuclear distances (see also Table 1). As a result of this behaviour the $1(1/2)_u$-level has a well pronounced maximum. On the other hand the direct relativistic effect which has the strong tendency to contract the wavefunction for higher Z tries to pull the radial crossing towards smaller internuclear distances. For the Yb-Yb system with $Z_u=140$ this effect becomes so strong that indeed the position of the radial crossing is pushed inwards and the energetic splitting between these levels decreases.

It is well known [12] that the spin-orbit effect for super-heavy systems near $Z\simeq 160$ becomes overwhelmingly large. This pushes the radial crossing again to larger internuclear distances as can be seen on the system Pb-Pb. The increase of the energy splitting in this very heavy system as compared to

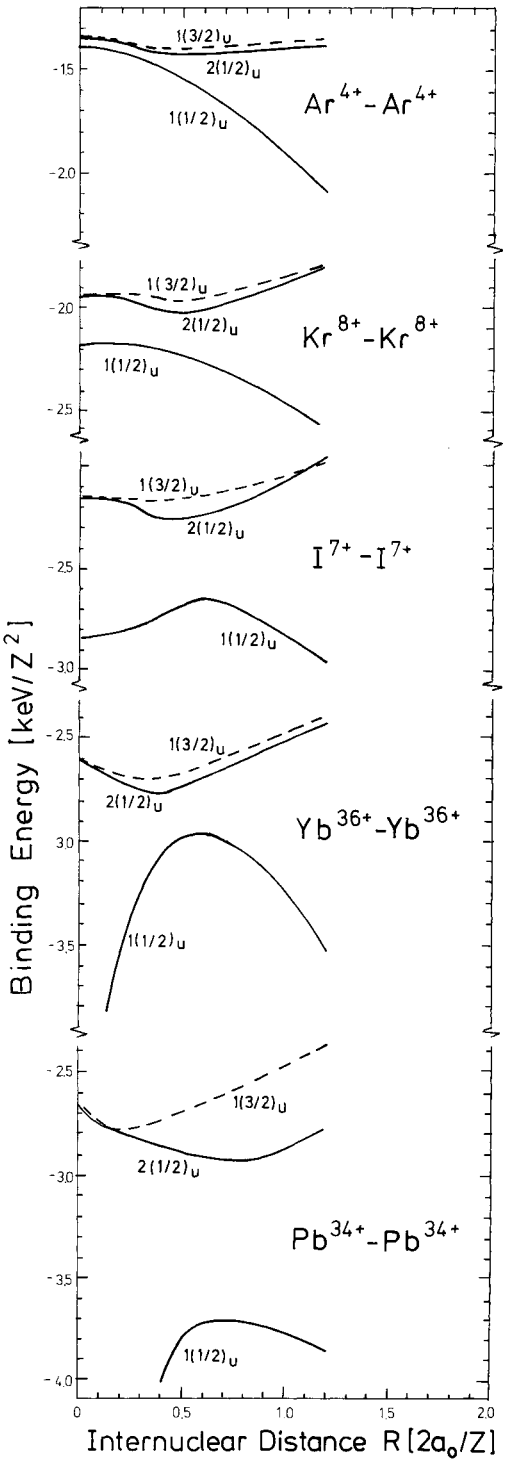

Fig. 2. Ab initio SCF level structure for the systems a) Ar-Ar ($Z_u=36$) b) Kr-Kr ($Z_u=72$) c) I-I ($Z_u=106$) d) Yb-Yb ($Z_u=140$) and e) Pb-Pb ($Z_u=164$) in scaled units

Table 1. Position R_x and Energy gap ΔE_x between the $1(1/2)_u$- and $2(1/2)_u$-levels for the systems Ar-Ar, Kr-Kr, I-I, Yb-Yb, and Pb-Pb

		$R_x(2a_0/Z)$	ΔE_x (eV/Z^2)
Ar-Ar	($Z_u=36$)	0.32	0.04
Kr-Kr	($Z_u=72$)	0.50	0.21
I-I	($Z_u=106$)	0.58	0.40
Yb-Yb	($Z_u=140$)	0.52	0.24
Pb-Pb	($Z_u=164$)	0.67	0.77

Yb-Yb mainly results from a many-body-effect. The direct relativistic effect contracts all molecular wavefunctions, which are strongly connected with atomic $j=1/2$ wavefunctions, dramatically. As a result a large number of electrons gather in the vincinity of the two nuclei at a distance of the 1(1/2) shell. These then shield those outer wavefunctions more strongly which are connected with atomic states with $j>1/2$. In accordance with atomic physics this can be called indirect relativistic effect in a molecule. This effect probably is the main reason for the relative small increase of the minimum of $2(1/2)_u$-level in Pb-Pb as compared to Yb-Yb.

This comparison definitely shows that there is no simple general trend for the behaviour of the levels involved when one proceeds to higher Z-systems. The same is expected to be true for the wavefunctions and matrix elements. Over the whole range of nuclear charges exists a delicate balance between the direct influence of the many-body screening and direct relativistic effects as well as the various indirect effects.

V. Comparison of Different Calculations of the System I-I

Up to now three other calculations exist for medium heavy systems namely I-I. Figure 3 compares the level scheme of the calculations of Anholt et al. [5], Jakubaßa et al. [6], and Müller et al. [13] with our results. Table 2 compares the position R_x and the energy gap ΔE_x of the avoided crossing of the $(1/2)_u$-levels in the various calculations of I-I. We expect that in the case of the calculations from [5] (dashed lines) the deviation relative to our results is caused by omitting all relativistic operators in the static Hamiltonian except the spin-orbit coupling. The discrepancies of the results obtained in [6] (dash-dotted lines) can be explained by the fact that the authors used united atom wavefunctions. These wavefunctions do not seem to be reasonable for the calculations at distances where the dynamic coupling occurs. They push the crossing point towards smaller internuclear distances and give an unreasonable raise in the slope of the $2(1/2)_u$-level. The maximum in the $1(1/2)_u$-level is by far too high which reduces the energy gap by more than 25% if

Table 2. Position R_x and Energy gap ΔE_x between the $1(1/2)_u$- and $2(1/2)_u$-levels in the system I-I

	$R_x(2a_0/Z)$	ΔE_x (eV/Z^2)
Ref. 13	1.3	0.72
Ref. 5	0.62	0.67
Ref. 6	0.47	0.31
This work	0.58	0.40

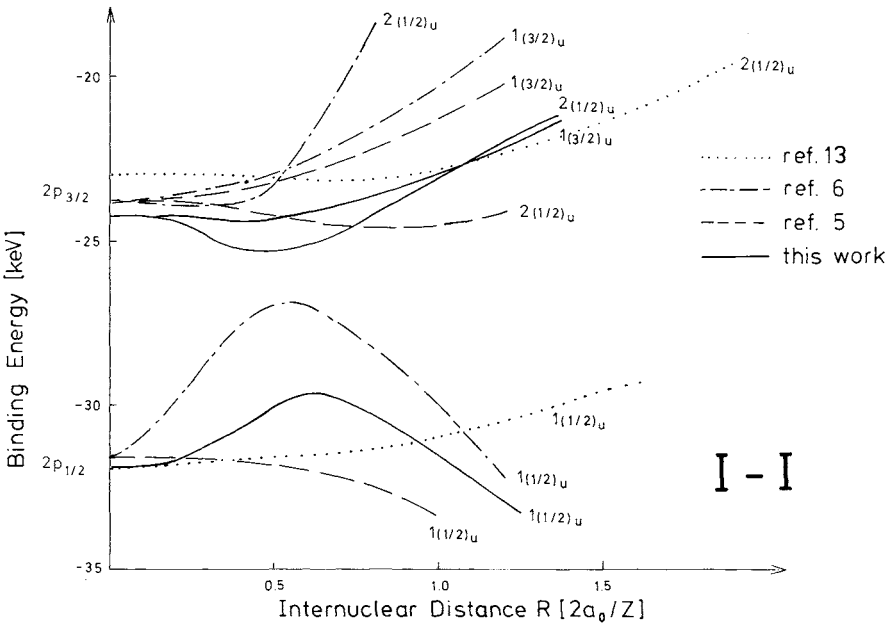

Fig. 3. Adiabatic correlation diagram for the system I-I in the region of the $n=2$ united levels. Dashed line [5], dash-dotted line [6], dotted line [13] lowered by 1 keV and full line this work

compared with our results. In both calculations [5] and [6] the $2(1/2)_u$- and $1(3/2)_u$-levels do not degenerate again as it should be due to physical reason discussed in part IV. In the case of [13] (dotted lines) we could not find any plausible explanation for the deviation from all three other results. Especially the $1(1/2)_u$-level does not show the expected peak structure.

In addition, we expect that the dynamic coupling elements calculated in [6] include the same range of uncertainty as the level structure due to the inappropriate wavefunctions.

A comparison of our level scheme and Table 2 with [5] shows the same crossing point R_x but a different energy gap. It is rather possible that the overestimation of the energy gap can be compensated by the correction function introduced in [5] which then results in a better agreement with the experimental values. This comparison shows that the results of the approximated calculations which were used up to now do not compare well with relative accurate self-consistent adiabatic calculations. In heavy systems the direct and indirect relativistic effects as well as the many-body effects as discussed in part IV are not small, so that only calculations which include the full relativistic Hamiltonian are expected to be a good basis for the interpretation of the experimental results.

VI. Conclusion

We have been able to present ab initio self-consistent DFS calculations for five symmetric systems from Ar-Ar to Pb-Pb. The results show that the level structure for the $2p_\pi - 2p_\sigma$ crossing is no simple function of Z_u. Various relativistic effects as well as many-body contributions have different influence at different Z_u. From a comparison with other calculations for the I-I system we have seen that a detailed description of the $2p_\pi - 2p_\sigma$ levels in large Z_u system has been far off from a detailed theoretical description.

Because results of coupled channel calculations sensitively depend on good coupling matrix elements we do not present here such calculations with any kind of model matrix elements. In a second paper we therefore plan to present coupled channel calculations with matrix elements calculated with the same order of sophistication and compare them with experimental K-vacancy production probabilities.

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