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MOMENT COUPLING IN THE INTERACTION OF ATOMS AND THEIR IONS WITH A $3d$-ELECTRON SHELL

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The moment coupling of an interacting ion and atom with a $3d$-electron shell is analyzed for the ground state of identical atoms and ions where resonant charge exchange proceeds with transition of a $4s$-electron. The interaction of the ion charge with the atom quadrupole moment is important for this system along with the exchange interactions and spin-orbital interactions inside an isolated atom and ion. The quadrupole moment for $3d$-atoms in the ground states is evaluated. The hierarchy of interactions in a molecular ion is analyzed depending on ion–atom distances and is compared with the standard Hund scheme. The resonant charge exchange proceeds effectively at separations corresponding to an intermediate case between cases "a" and "c" of the Hund coupling scheme.

1. INTRODUCTION

The coupling of electron moments in atoms, ions, and molecules determines their quantum numbers, which are responsible for the behavior of these atomic particles in various processes of their interactions and collisions. General principles of moment coupling are based on spectroscopic data and were formulated for atoms [1] and molecules [2, 3] at the stage of creation of the quantum mechanics. Our understanding of these problems has expanded with an increase in our experience in atomic physics. In particular, the study of resonant charge exchange of light atoms and their ions with filling p-shells [4–7] allows revising the Hund scheme of moment coupling in molecules. In this paper, we analyze coupling in molecular ions of elements of the iron period, being guided by distances between an ion and the parent atom that are responsible for the resonant charge exchange process.

It is important that the moment coupling for weakly interacting ion and atom also determines the cross section of this process. We demonstrate this with a simple example. As follows from Table 1, the configuration of electron shells for a $3d$-atom and ion differs by the addition of one s-electron to the ion in most cases. It may seem that the charge exchange process can be considered in this case as the s-electron transition between two structureless cores. But this takes place if the ion–atom exchange interaction significantly exceeds the quadrupole ion–atom interaction at distances that give the main contribution to the cross section of resonant charge exchange. For different relative strengths of these two interactions, the cross section may be less by an order of magnitude.

This requires analyzing the hierarchy of ion–atom interactions. In the absence of nuclear motion, we have three types of interactions for the ion and atom with a given orbital moment and spin: the molecular ion consisting of an ion and the parent atom, with spin-orbital interaction of the atomic ion and the atom, the quadrupole interaction of the ion charge with the atom, and the ion–atom exchange interaction at large separations. It can be seen that the classical Hund scheme [2, 3] is not suitable in this case because we have two types of electrostatic interaction (quadrupole and exchange ones). Below, we therefore analyze the hierarchy of interactions for an ion and the parent atom for the iron period elements.

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Table 1. Electron shells and electron terms for atoms and ions with a filled $3d$-electron shell in the ground states, and the ionization potential as the electron binding energy with ion formation in the ground state [8, 9]. The asterisk marks electronically excited states of an atom or ion

Element number	Element	Atom shell	Transferred electron	Atom term	Ion term	I_0, cm^{-1}	B, cm^{-1}	b, cm^{-1}
21	Sc	$3d4s^2$	s	^2D	^3D	52922	36	17.4 ± 0.4
21	Sc	$3d^24s$	d	$^4F^*$	^3D	41402	7.50 ± 0.02	17.4 ± 0.4
22	Ti	$3d^24s^2$	s	^3F	^4F	55000	27.9 ± 0.3	18.8 ± 0.1
22	Ti	$3d^34s$	d	$^5F^*$	^4F	48443	10.4 ± 0.2	18.8 ± 0.1
23	V	$3d^34s^2$	s	^4F	$^5F^*$	56964	27.1 ± 0.4	20.3 ± 0.3
24	Cr	$3d^54s$	s	$^7S_3$	$^6S_{5/2}$	54570	0	0
24	Cr	$3d^54s$	d	$^7S_3$	$^6D^*$	66512	0	23.0 ± 0.6
25	Mn	$3d^54s^2$	s	$^6S_{5/2}$	$^7S_3$	59959	0	0
26	Fe	$3d^64s^2$	s	^5D	^6D	63740	-50 ± 1	-46.5 ± 0.7
27	Co	$3d^74s^2$	s	^4F	$^5F^*$	66751	-89 ± 3	-57.0 ± 0.8
28	Ni	$3d^84s^2$	s	^3F	^2D	61600	-162 ± 4	-50.2
29	Cu	$3d^{10}4s$	s	$^2S_{1/2}$	$^1S_0$	62317	0	0
29	Cu	$3d^{10}4s$	d	$^2S_{1/2}$	$^3D^*$	84246	0	-153

2. MOMENT COUPLING IN ATOMS AND IONS WITH THE 3d-ELECTRON SHELL

The interaction between an ion and the parent atom at large separations can be divided into three types — spin–orbit, quadrupole, and exchange interactions — and our task is to construct the hierarchy of these interactions in each particular case and to determine the quantum numbers of the molecular ion under these conditions. Because the spin-orbital interaction for the ion and atom inside the molecular ion is the same as when the ion and atom are separated, we use the spectroscopic data [8, 9] for spin-orbital interactions in these atoms and ions. In principle, these atoms and ions are many-electron systems, where electrons are located in the Coulomb field of the nucleus. Based on the one-electron approximation, where electrons are located in a self-consistent field of the nucleus and other electrons, and using the Pauli principle, we can reduce the character of the electron distribution in the nucleus Coulomb field to the shell atom scheme [10, 11]. Below, we consider atoms and ions with $4s^k3d^n$ atomic shells.

The next approximation in this analysis is the summation of the moments of individual electrons of this electron shell into the total orbital moment L of electrons and the total electron spin S, which are quantum numbers of atoms (or ions) [10, 11]. These quantum numbers may be applicable if the relativistic interactions are ignored. If the relativistic interactions are taken into account, then in addition to the above quantum numbers L and S, the total moment J is also an atom quantum number, and hence L, S, J, M_J are the atom quantum numbers (M_J is the projection of the total atom moment onto a given direction).

Table 1 contains the spectroscopic energy data for the ground state quantum numbers of atoms and ions of the iron period elements [8, 9]. We introduce the atom ionization potential I with ion formation in a given state as

$$I = I_0 - E_J + E_j, \tag{2.1}$$

where I_0 is the atom ionization potential for the lowest-energy values of the atom, J and ion j total moments at given electron shells and quantum numbers $LSls$, and E_J and E_j are the excitation energies for the indicated values of the atom and ion moments. The atom ionization potential I characterizes the binding energy of a transferred electron if we regard charge exchange resulting from the electron transition from one core to another one as a resonant process. The parameters of atom and ion spectra in formula (2.1) are taken from [8, 9]. The excitation energies E_J and E_j of an atom and ion with the total moments J and j can be approximated as [12]

$$
\begin{gathered}
E_J = BJ(J+1) - BJ_0(J_0+1), \\
E_j = bj(j+1) - bj_0(j_0+1),
\end{gathered}
\tag{2.2}
$$

where J_0 and j_0 are the total moments for the ground atom and ion states. The values of the parameters B and b and their accuracy follow from the spectroscopic data [8, 9].

The data in Table 1 justify the Hund rules [1, 12], according to which the ground state of an atom or ion with a given electron shell is characterized by the maximum spin due to the exchange interaction between electrons, and among the states with the maximum spin, the maximum orbital number corresponds to the atom or ion ground state. As regards the total moment, it is minimal if the shell is less than half-filled and maximal if the filling is above one half. We note that just the analysis of atoms and ions of the iron group of the periodical system of elements (from scandium to nickel) allowed Hund [1] to formulate the rules for the hierarchy of atom and ion energy levels. One more aspect of the Hund rules relates to the sequence of fine levels according to which excitation of fine levels corresponds to an increase in the total moment if the electron shell is less than half-filled, and to a decrease in the total momentum otherwise.

Table 2 gives the lowest electron levels for the vanadium atom and ion and also for the cobalt atom and ion [8, 9, 13] as examples of atoms and ions with filling d-shells. The analysis of these data exhibits the validity of the LS scheme of moment coupling because the energy difference for states with the same value of the orbital and spin moments is small compared to the energy distance between the neighboring levels of different L and S. Next, there is competition between $3d$- and $4s$-states. For this reason, the states of a given atom or ion with a different number of $4s$- and $3d$-electrons are alternated. Moreover, there is a mixing of states with different electron shells in the case of an excited vanadium ion, as well as for more excited states of other atoms and ions. This competition is important for the resonant charge exchange process.

Table 2 also exhibits that the exchange interaction between s- and d-shells in the cases considered is 4000–6000 cm^{-1} and is small compared to the splitting energy for states of this d-shell. This exchange interaction is characterized by the energy difference for the states of an atom or ion with one $4s$-electron and different total spins at the same total moment of the d-electron shell.

3. INTERACTION BETWEEN AN ION AND THE PARENT ATOM WITH A 3*d*-SHELL

Our goal is to analyze the character of moment coupling for molecular ions consisting of an ion of the iron group and the parent atom at large distances between them. We are guided by distances that determine the cross section of resonant charge exchange in collisions of these ions and atoms. This process occurs at large distances between the ion and the atom compared to atomic sizes, where the ion–atom interaction is weak. This allows separating various types of interactions and constructing a hierarchy of interactions in this molecular ion.

In view of the hierarchy of the interaction potentials for an atom and its ion if the distance R between them is large, we represent the ionization potential I of a transferred electron based on formula (2.1),

$$
I(R) = I = I_0 - E_J + E_j + \frac{eq_M}{R^3} \pm \frac{1}{2}\Delta(R), \tag{3.1}
$$

where $I_0(LSls)$ is the atom ionization potential if the atom and ion are separated and are in the states with the given values of the atom moment L and spin S and the same quantum numbers ls for the ion; the energies E_J and E_j correspond to excitation of the atom with the total moment J and the ion with the total moment j with respect to the lowest-energy states with the total moments J_0 and j_0 for the isolated atom and ion; q_M is the atom quadrupole moment if M is the atom orbital moment; and $\Delta(R)$ is the ion–atom exchange interaction potential resulting from the electron transition from one atomic core to another, with the + sign corresponding to an even state of the molecular ion, and the − sign corresponding to an odd state with respect to reflection of electrons with respect to the symmetry plane that is perpendicular to the molecular axis and bisects it. In this consideration, we restrict ourselves to the exchange interaction inside the atom and ion, and therefore LS and ls (the orbital moments and spins of the atom and ion) are their quantum numbers, and the orbital moments and spins are summed into the total moments J and j of the atom and ion in the framework of the LS-coupling scheme. Therefore, formula (3.1) corresponds to a certain hierarchy of molecular energies. Practically, $I(R)$ is the molecular ion energy at large ion–atom separations, and we count this energy from the ground state of two noninteracting atomic particles.

In formula (3.1), the interaction of the ion charge with the atom quadrupole moment is the basic electrostatic ion–atom interaction at large separations. We

Table 2. Positions of the lowest levels for vanadium and cobalt atoms and ions. J is the value of the total momentum of the atomic particle, n_J is the number of such states, E is the excitation energy of the lowest state from the group with a given LS, ΔE is the difference between the energies of the lowest and highest states of this group

Atom, ion	Configuration	Term	J	n_J	E, cm^{-1}	ΔE, cm^{-1}
V I	$3d^3 4s^2$	a^4F	3/2–9/2	4	0	553
	$3d^4(^5D)4s$	a^6D	1/2–9/2	5	2112	313
	$3d^4(^5D)4s$	a^4D	1/2–7/2	4	8413	304
	$3d^3 4s^2$	a^4P	1/2–5/2	3	9544	280
	$3d^3 4s^2$	a^2G	7/2–9/2	2	10892	208
	$3d^3 4s^2$	a^2P	3/2–1/2	2	13801	9.4
	$3d^3 4s^2$	a^2D	3/2–5/2	2	14515	34
	$3d^4(^3H)4s$	a^4H	7/2–13/2	4	14910	163
V II	$3d^4$	a^5D	0–4	5	0	339
	$3d^3(^4F)4s$	a^5F	1–5	5	2605	558
	$3d^3(^4F)4s$	a^3F	2–4	3	8640	458
	$3d^4$	a^3P	0–2	3	11296	613
	$3d^4$	a^3H	4–6	3	12545	161
	$3d^4$	b^3F	2–4	3	13491	118
	$3d^3(^4P)4s$	a^5D	1–3	3	13512	230
	$3d^4 + 3d^3(^2G)4s$	a^3G	3–5	3	14462	194
Co I	$3d^7 4s^2$	a^4F	3/2–9/2	4	0	1809
	$3d^8(^3F)4s$	b^4F	9/2–3/2	4	3483	1593
	$3d^8(^3F)4s$	a^2F	7/2–5/2	2	7442	1018
	$3d^7 4s^2$	a^4P	5/2–1/2	3	13796	604
	$3d^8(^3P)4s$	b^4P	5/2–1/2	3	15184	111
	$3d^7 4s^2$	a^2G	9/2–7/2	2	16468	766
	$3d^8(^1D)4s$	a^2D	3/2–5/2	2	16471	309
	$3d^8(^3P)4s$	a^2P	3/2–1/2	2	18390	385
Co II	$3d^8$	a^3F	4–2	3	0	1597
	$3d^7(^4F)4s$	a^5F	5–1	5	3351	1854
	$3d^7(^4F)4s$	b^3F	4–2	3	9813	1509
	$3d^8$	a^1D	2	1	11651	–
	$3d^8$	a^3P	2–0	3	13261	333
	$3d^7(^4P)4s$	a^5P	3–1	3	17772	567
	$3d^8$	a^1G	4	1	19190	–
	$3d^7(^2G)4s$	a^3G	5–3	3	21625	790

derive this part of the interaction potential from a general formula that allows finding the expression for the atom quadrupole moment. If an ion that is rerarded as a charge $+e$ locate at the ion point, and the atom valence electrons are at large separations R, then their interaction potential is given by

$$V(R) = \frac{ke^2}{R} - \sum_i^k \frac{e^2}{|\mathbf{R}-\mathbf{r}_i|} = \sum_i^k \sum_{n=2}^{\infty} \left(\frac{r_i}{R}\right)^n P_n(\cos\theta_i),$$

where $\mathbf{r}_i$ is the coordinate of ith valence electron, θ_i is the angle of the radius vector of this electron with respect to the axis joining the charge and the atom nucleus, and k is the number of valence electrons. Expanding this formula in the reciprocal ion–atom distances R, we can represent the second term of this interaction, the ion–atom quadrupole interaction, in the form

$$V = -\frac{e\widehat{q}}{2R^3}\,, \tag{3.2}$$

where the quadrupole moment operator is [14]

$$\widehat{q} = \sum_i^k r_i^2 P_2(cos\theta_i). \tag{3.3}$$

We note that because the quadrupole moment operator is independent of the spin coordinate in the framework of the LS coupling scheme of the atom, it depends on the quantum numbers LM (the orbital moment and its projection onto the molecular axis). Assuming the atom quadrupole moment to be determined by valence electrons, we have its matrix elements

$$\langle LM|\widehat{q}|LM'\rangle = q_{LM}\delta_{MM'},\; q_{LM} = \langle LM|\widehat{q}|LM\rangle,$$

and

$$q_{LM} = q_{L,-M}.$$

Because the atom is isotropic on average, we have the relation

$$\sum_{M=-L}^{L} q_{LM} = 0. \tag{3.4}$$

Accordingly, the quadrupole moment is zero for an atom with $L = 0$.

The total number of valence electrons for an atom with a completed electron shell having the moment l is $n = 2(2l + 1)$. We can compare the quadrupole moments for an atom with a given electron shell and an atom with the same number k of electrons and holes, i. e., for the atoms with k and $2(2l + 1) - k$ electrons. We have

$$q_{LM}(k) = -q_{L,M}(4l + 2 - k).$$

If a valence electron is in the field of a structureless core, formula (3.3) gives [14]

$$q_{lm} = 2\left\langle r^2 P_2\cos\theta\right\rangle = 2\frac{3m^2 - l(l+1)}{(2l-1)(2l+3)}\,\overline{r^2}, \tag{3.5}$$

where l and m are the electron moment and its projection onto the axis and $\overline{r^2}$ is the average square of the electron orbit radius. Hence, because the quadrupole moment operator for the electron shell is

$$\widehat{q} = \sum_{i=1}^{k}\widehat{q}_i,$$

where $\widehat{q}_i$ is the quadrupole moment operator for the ith electron, formula (3.5) gives the atom quadrupole moment in the one-electron approximation [14] as

$$q_{LM} = 2\sum_i^k \frac{3m_i^2 - l(l+1)}{(2l-1)(2l+3)}\,\overline{r^2} \tag{3.6}$$

in the case where the electron shell contains k valence electrons with an orbital moment l. This formula holds only in the case where the atom electrons are characterized by a certain combination of the moment projections m_i, such that the atom wave function consists of only one coordinate wave function rather than their combination [12].

It is convenient to introduce the reduced quadrupole moment Q_{LM} using the relation

$$q_{LM} = \frac{2\overline{r^2}}{(2l-1)(2l+3)}Q_{LM}. \tag{3.7}$$

Below, we apply this formula to an atom with valence d-electrons, where

$$q_{LM} = \frac{2\overline{r^2}}{21}\cdot Q_{LM} \tag{3.8}$$

and in the one-electron approximation,

$$Q_{LM} = \sum_{i=1}^{k}(3m_i^2 - 6). \tag{3.9}$$

The reduced quadrupole moment also satisfies the relations

$$Q_{LM} = Q_{L,-M},\quad \sum_M Q_{LM} = 0. \tag{3.10}$$

In addition, we can relate the quadrupole moment for any momentum projection to that at the projection momentum coincident with the moment, namely, [12]

$$Q_{LM} = Q_{LL}\frac{3M^2 - L(L+1)}{L(2L-1)}. \tag{3.11}$$

We are based on the one-electron approximation, and therefore the wave function for valence electrons is a combination of Slater determinants [11, 15–17], which include the one-electron wave functions of valence electrons. Then formula (3.9) holds if the electron wave function for valence electrons is determined by a single Slater determinant. This pertains to quadrupole moments Q_{LL} if an atom has the maximum projection of the total orbital moment or spin if these projections of moments have the maximum possible values. For the states $d^2(^3F)$, $d^2(^1G)$, and $d^3(^4F)$, Q_{LL} takes the respective values 3, 12, and 3. In particular, for the electron shell $d^3(^4F)$, we use formula (3.9) to obtain the atom quadrupole moment

$$\begin{gathered} Q_{33}=3, \quad Q_{32}=0, \\ Q_{31}=-9/5, \quad Q_{30}=-12/5. \end{gathered} \tag{3.12}$$

These values satisfy relations (3.10).

If the wave function of valence electrons in the one-electron approximation cannot be represented as a single Slater determinant, then finding the atom quadrupole moment becomes complicated. It may seem that because the quadrupole moment operator in (3.3) is the sum of one-electron operators, it is convenient to use the parentage scheme for the wave function of valence electrons by representing it in the form [11, 19–21]

$$\Psi_{LSM_LM_S}(1,2,\ldots,k)=\frac{1}{\sqrt{k}}\hat{P}\sum_{l,m_l,s,m_s,\mu,\sigma}G_{ls}^{LS}(l_e,k),$$

$$\left[\begin{array}{ccc} l_e & l & L \\ \mu & m_l & M_L \end{array}\right]\left[\begin{array}{ccc} \frac{1}{2} & s & S \\ \sigma & m_s & M_S \end{array}\right]\times$$
$$\times\,\Psi_{lsm_lm_s}(1,\ldots,k-1)\psi_{l_e\frac{1}{2}\mu\sigma}(1),$$

where k is the number of a valence electron, the operator $\hat{P}$ permutes positions and spins of a test valence electron and other valence electrons, $LSMM_S$ are atom quantum numbers (the atom angular moment, the atom spin and projections of these moments onto a quantizations axis), lsm, m_s are similar quantum numbers of an atomic core, $l_e\frac{1}{2}, \mu\sigma$ are the indicated quantum numbers of an extracted valence electron, and $G_{ls}^{LS}(l_e,k)$ is the fractional parentage coefficient or the Racah coefficient [19], which is responsible for electron coupling with the atomic core in forming the atom. Because of the permutation of electrons, the quadrupole moment due to a given electron is the sum of the quadrupole moment of an extracted electron and of the atomic core. In this case, the requirement is that because of the Pauli principle, the wave function of the core electron must not coincide with that of an extracted electron, and this complicates evaluation of the atom quadrupole moment and makes this scheme nonproductive. It is more pragmatic to construct the wave function of valence electrons as a combination of Slater determinants, and this is a complicated operation.

Table 3. The reduced quadrupole moments Q_{LM} for atoms with the $3d^2$-electron shell

Electron term	$M=0$	$M=1$	$M=2$	$M=3$	$M=4$
$(3d^2)^1S$	0	–	–	–	–
$(3d^2)^3P$	42/5	−21/5	–	–	–
$(3d^2)^1D$	18/7	9/7	−18/7	–	–
$(3d^2)^3F$	−12/5	−9/5	0	3	–
$(3d^2)^1G$	−60/7	−51/7	−24/7	3	12

We use the above formulas for atoms with two valence d-electrons (or holes), i. e., in the case where the atom has the d^2-electron shell. We can then separate space and spin coordinates because the quadrupole moment is independent of spin coordinates. Then the space wave function $\Psi_{LSM}(1,2)$ of this atom is given by

$$\Psi_{LM}=\sum_m\left[\begin{array}{ccc} 2 & 2 & L \\ m & M-m & M \end{array}\right]\times$$
$$\times\,\psi_{2m}(1)\psi_{2,(M-m)}(2), \tag{3.13}$$

where the arguments of the wave functions indicate the numbers of electrons. From this, we obtain the reduced quadrupole moment of the two-electron atoms with d valence electrons as

$$Q_{LM}=\sum_m(6m^2+3M^2-6mM-12)\times$$
$$\times\left[\begin{array}{ccc} 2 & 2 & L \\ m & M-m & M \end{array}\right]^2. \tag{3.14}$$

Table 3 contains the quadrupole moments of atoms with the d^2-valence electron shell. We note that because the two-electron wave function changes sign as a result of an exchange of electrons, the electron states with an even total orbital moment L are characterized by the spin $S=0$, and correspond to odd orbital moments L $S=1$. Next, the quadrupole moment is an even function of M, and therefore we restrict ourself below to the case $M\geq 0$. Of course, the values in Table 3 satisfy relations (3.10) and (3.11). We note that the reduced quadrupole moments Q_{LM} for the $3d^3(^4F)$ and $3d^2(^4P)$ states under consideration coincide.

Table 4. The reduced quadrupole moments Q_{LM} for atoms with $3d$-valence electrons for the lowest electron states given in Table 1

Atom, shell, electron term	Q_0	Q_1	Q_2	Q_3	$\overline{r^2}/a_0^2$
Sc $(3d4s^2)(^2D)$	6	3	–6	–	16.2
Sc $(3d^24s)(^4F)$	6	3	–6	–	21.3
Ti $(3d^24s^2)(^3F)$	$-12/5$	$-9/5$	0	3	14.2
Ti $(3d^34s)(^5F)$	$-12/5$	$-9/5$	0	3	16.8
V $(3d^34s^2)(^4F)$	$-12/5$	$-9/5$	0	3	12.8
Cr $(3d^54s)(^7S_3)$	0	–	–	–	13.0
Mn $(3d^54s^2)(^6S_{5/2})$	0	–	–	–	11.0
Fe $(3d^64s^2)(^5D)$	-6	-3	6	–	9.9
Co $(3d^74s^2)(^4F)$	$-12/5$	$-9/5$	0	3	8.8
Ni $(3d^84s^2)(^3F)$	$-12/5$	$-9/5$	0	3	9.8
Cu $(3d^{10}4s)(^2S_{1/2})$	0	–	–	–	9.5

Table 5. The reduced quadrupole moments Q_{LSJM_J} for atoms with the $3d^3$-electron shell

$M_J\backslash J$	3/2	5/2	7/2	9/2
1/2	$-36/25$	$-198/175$	$-10/7$	-2
3/2	36/25	$-99/350$	$-6/7$	$-3/2$
5/2	–	99/70	2/7	1/2
7/2	–	–	2	1
9/2	–	–	–	3

The above results give the values for the atom quadrupole moments for the ground states listed in Table 1. The quadrupole moments of the ground states of atoms of the iron group of the periodical system are represented in Table 4. We take into account that the addition of an s-electron to a d^n-shell does not change the atom quadrupole moment, and the values $\overline{r^2}$ in Table 4 are taken from [18].

4. HIERARCHY OF ION–ATOM INTERACTIONS AT LARGE SEPARATIONS

The above analysis is applicable if the quadrupole ion–atom interaction significantly exceeds the fine splitting of atom levels that corresponds to the quantum numbers

$$LMSJlsjm_j \tag{4.1}$$

of the weakly interacting ion and atom, where L, M, S, and J are the atom orbital moment its projection on the molecular axis, the atom spin, and the total atom moment and l, s, j, and m_j are the ion orbital moment the ion spin, the total atom moment and its projection onto the molecular axis. If the ion–atom quadrupole interaction is relatively small, then the quantum numbers are

$$LSJM_Jlsjm_j, \tag{4.2}$$

where M_J and m_j are the projections onto the molecular axis for the total atom and ion moments. The reduced atom quadrupole moments in the basis $LSJM_J$ can be related to those in the basis $LMSJ$ as [12]

$$Q_{LSJM_J} = \sum_M \begin{bmatrix} L & S & J \\ M & M_J - M & M_J \end{bmatrix}^2 Q_{LM}. \tag{4.3}$$

We note that the reduced quadrupole moment in basis (4.2) has the identical symmetry properties as the moment in (3.10),

$$Q_{J,M_J} = Q_{J,-M_J}, \quad \sum_{M_J} Q_{JM_J} = 0. \tag{4.4}$$

The quadrupole moments in basis (4.2) are related as [12]

$$Q_{J,M_J} = Q_{J,J}\frac{3M_J^2 - J(J+1)}{J(2J-1)}. \tag{4.5}$$

In addition, the maximum moment projections in bases (4.2) and (4.1) are related as

$$\begin{gathered} Q_{J,J} = Q_{L,L}\frac{3\lambda(2\lambda-1)-2J(J+1)L(L+1)}{(J+1)(2J+3)L(2L-1)}, \\ \lambda = \langle \widehat{\mathbf{J}}\widehat{\mathbf{L}} \rangle = [J(J+1)+L(L+1)-S(S+1)]/2. \end{gathered} \tag{4.6}$$

Table 5 lists the reduced quadrupole moments of an atom with the $3d^3$-electron shell in basis (4.2). The validity of this formula can be verified for any value in Table 5.

We now construct the hierarchy of energy levels for an ion interacting with its parent atom. The quasimolecule states can be divided into groups such that each group is characterized by certain quantum numbers $LSls$. This means that according to the behavior of energy levels for atoms and ions of the iron group of the periodical system of elements [8, 9], the energy difference for the states with different values of the quantum numbers $LSls$ is large compared to the states with different quantum numbers Jj for the same values $LSls$. The fine splitting of atom and ion levels

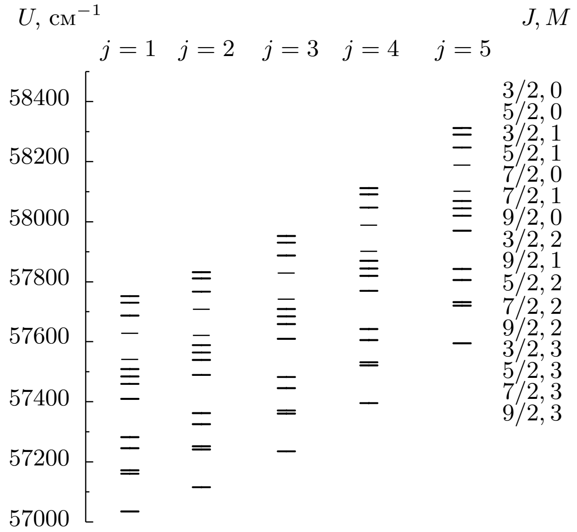

Fig. 1. Electron terms (ionization potentials) for the quasimolecule $V(3d^34s^2,{}^4F)+V^+(3d^3({}^4F)4s^5F)$ expressed in cm^{-1} at the ion–atom separation $R=10a_0$ in accordance with formula (3.1). Electron terms are given in basis (4.1), and the sequence of valid quantum numbers for energy levels for electron terms is given on the right, and energies of some levels coincide; the splitting due to the exchange ion–atom interaction is ignored

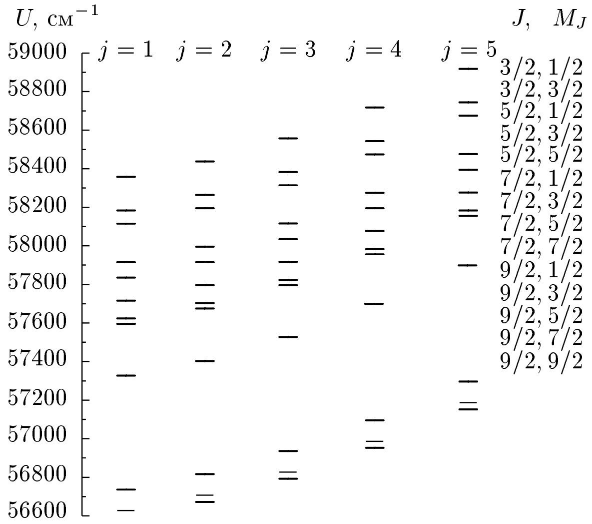

Fig. 2. Electron terms (ionization potentials) for the quasimolecule $V(3d^34s^2,{}^4F)+V^+(3d^3({}^4F)4s^5F)$ expressed in cm^{-1} at the ion–atom separation $R=20a_0$ in accordance with formula (3.1). Electron terms are given in the basis (4.2), and the sequence of valid quantum numbers for energy levels for electron terms is given on the right, and energies of some levels coincide; the splitting due to the exchange ion–atom interaction is ignored

may be comparable with the quadrupole ion–atom interaction in the range of ion–atom separations under consideration. Figures 1 and 2 contain the positions of electron terms for vanadium ions and their parent atoms for the ground ion and atom states at distances $R=10a_0$ and $R=20a_0$. In Figs. 1 and 2, we give the spectra of the interacting vanadium atom and ion in the case where the atom electron shell results from joining an s-electron to the ion electron shell. Then $L=l$ and $S=s+1/2$. At the separation $R=10a_0$ in Fig. 1, the scheme of quantum numbers in (4.1) is realized, and Fig. 2 with the separation $R=20a_0$ corresponds to scheme (4.2), where the quadrupole ion–atom interaction potential is small compared to the fine level splitting for the ion and atom. In intermediate cases where the spin–orbit interaction is comparable to the quadrupole ion–atom interaction, the positions of the molecular levels may be found by the standard method [12] of solving the secular equation that includes the quadrupole and spin–orbit interactions. We previously used this operation for oxygen and nitrogen [6, 7], where the atom quadrupole moment is determined by valence p-electrons.

Restricting to the case of the vanadium ion and atom in Figs. 1, 2, we analyze the transition from scheme (4.1) to (4.2). For definiteness, we compare the energy gaps between energy levels for states with the quantum numbers JM (J is the atom total moment and M is the orbital moment projection onto the molecular axis) for neighboring values of J and M. The energy gap between levels with quantum numbers $9/2, 3$ and $9/2, 2$ is equal to the energy gap between levels with quantum numbers $9/2, 3$ and $7/2, 3$ at the separation $R=14a_0$. Separations of this order of magnitude characterize the transition from quantum numbers (4.1) to quantum numbers (4.2) for vanadium, as R increases from approximately $R=10a_0$ to $R=20a_0$. We also note that at $R=10a_0$ (Fig. 3), the second upper level is coupled to the third one, and the forth upper level is coupled to the fifth one, but this does not affect the general form of the spectra. In addition, levels with neighboring values of $LSls$ are almost uncoupled.

5. COUPLING OF ELECTRON MOMENTS IN RESONANT CHARGE EXCHANGE

Our goal is to construct the interaction potential of an ion and its parent atom at large distances between these particles, in the case where these distances determine the cross section of the resonant charge ex-

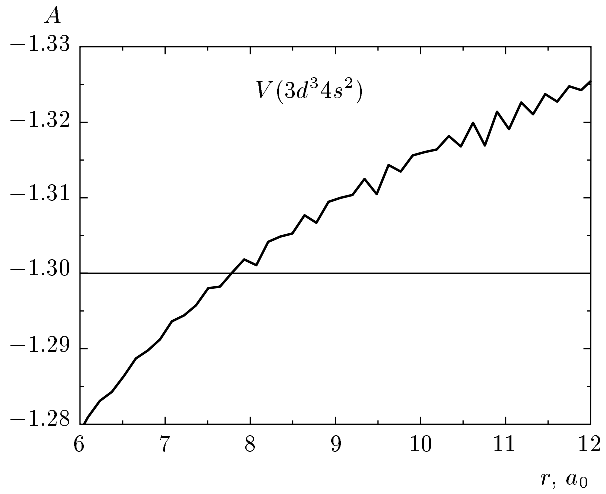

Fig. 3. The asymptotic coefficient A for a $4s$-electron of the vanadium atom. As can be seen, as a result of approximating the numerical wave function by asymptotic expression (5.2) in the region $(6\div 12)a_0$, we obtain $A = 1.30 \pm 0.02$

change process in slow ion–atom collisions. Then together with the electrostatic interaction between these particles, which is determined mostly by the ion interaction with the quadrupole atom moment, we take the exchange ion–atom interaction into account, which is determined by electron transfer from one atomic core to another. This exchange interaction is responsible for the resonant charge exchange whose nature consists in the interference of even and odd states of the molecular ion consisting of an ion and an atom [22]. Then the exchange ion–atom interaction potential $\Delta(R)$ at a given separation R is the energy difference for the even and odd states with respect to reflection of all electrons at this separation with respect to the symmetry plane that bisects the axis joining the nuclei and is perpendicular to this axis.

We focus on the interaction of the ion and atom in the ground state for elements of the iron group of the periodical system, where the ion and atom electron shells differ by one $4s$-electron (see Table 1). This results from competition between $3d$- and $4s$-electron shells for atoms and ions of this group and simplifies our analysis. Therefore, restricting ourselves to the interaction of atoms and ions in the ground states with $3d$-electron shells, we obtain that the exchange interaction potential is determined by the transition of an s-electron and is given by a formula in [23] for structureless cores,

$$\Delta_s(R) = A^2 R^{2/\gamma - 1} \exp(-R\gamma - 1/\gamma), \qquad (5.1)$$

where we use the atomic units for simplicity, the parameter γ is related to the atom ionization potential I as $I = \gamma^2/2$, and the parameter A characterizes the asymptotic behavior of the wave function for a valence electron. As a function of the distance r from the core, the electron radial wave function $R(r)$, if it is normalized to unity, is equal to

$$R(r) = A r^{1/\gamma - 1} \exp(-r\gamma) \qquad (5.2)$$

far from the core. We note that formula (5.1) is identical for atoms with $4s$- and $4s^2$-electron shells.

Formula (5.1) describes the case where the atom and ion states differ by one s-electron. According to Table 1, this applies to almost all elements of the iron group of the periodical system except the cases with a d^3-electron shell (or a d^3-hole shell). In this case, the ion–atom exchange interaction is zero in the framework of transitions of one electron, and the cross section of resonant charge exchange is small compared to that resulting from transitions of one electron. But the lowest excited state of an ion with a low excitation energy, as follows from Table 1, permits the one-electron exchange interaction, and just such transitions are taken into account in the ion–atom exchange interaction.

Table 6 contains the parameters of formula (5.1) that are of interest for the resonant charge exchange process involving atoms and ions with $3d$-electron shells in the ground states, where the exchange process results from transition of a $4s$-electron. We obtain the values of the asymptotic coefficient A for the transferred s-electron using the standard method [23, 24] of matching asymptotic wave function (5.2) with that obtained from a numerical solution of the Schrödinger equation [25]. An example of this matching for the vanadium atom is given in Fig. 3. We here define the asymptotic coefficient $A(r)$ in accordance with formula (5.2), and the accuracy for the average value of this parameter is determined by its values in the range from $r = 4/\gamma$ to $8/\gamma$.

We can calculate the cross section of resonant charge exchange using the asymptotic formula that has the following form in the two-state approximation for the transition of an s-electron between two structureless cores [22–24]:

$$\sigma_{res} = \frac{\pi R_0^2}{2}, \quad \frac{\Delta(R_0)}{v}\sqrt{\frac{\pi R_0}{2\gamma}} = \frac{e^{-C}}{2} = 0.28, \qquad (5.3)$$

and we use the atomic units. We assume the parameters of the cores to be identical in this process. Table 6 contains the values of the parameter R_0 according to formula (5.3) the ion energy of 1 eV for a motionless

Table 6. Parameters of a transferred s-electron in the resonant charge exchange process for atoms and ions with $3d$-electron valence shells

Element number	Element	Atom shell	Atom state	Ion state	γ	A	R_0/a_0	$\Delta(R_0)$, cm^{-1}
21	Sc	$3d4s^2$	${}^2D$	${}^3D$	0.694	1.31 ± 0.02	22	10.3
22	Ti	$3d^2 4s^2$	${}^3F$	${}^4F$	0.708	1.28 ± 0.01	21	10.4
23	V	$3d^3 4s^2$	${}^4F$	${}^5F^*$	0.720	1.30 ± 0.02	20	10.4
24	Cr	$3d^5 4s$	${}^7S_3$	${}^6S_{5/2}$	0.705	1.16 ± 0.02	22	9.7
25	Mn	$3d^5 4s^2$	${}^6S_{5/2}$	${}^7S_3$	0.694	1.32 ± 0.02	22	9.4
26	Fe	$3d^6 4s^2$	${}^5D$	${}^6D$	0.762	1.39 ± 0.02	19	10.5
27	Co	$3d^7 4s^2$	${}^4F$	${}^5F^*$	0.780	1.50 ± 0.02	18	10.6
28	Ni	$3d^8 4s^2$	${}^3F$	${}^2D$	0.749	1.28 ± 0.02	19	10.1
29	Cu	$3d^{10} 4s$	${}^2S_{1/2}$	${}^1S_0$	0.754	1.29 ± 0.02	19	9.8

Table 7. The cases of Hund coupling [2, 3, 12]

Hund case	Relation	Quantum numbers
a	$V_e \gg \delta_f \gg V_{rot}$	Λ, S, S_n
b	$V_e \gg V_{rot} \gg \delta_f$	Λ, S, S_N
c	$\delta_f \gg V_e \gg V_{rot}$	Ω
d	$V_{rot} \gg V_e \gg \delta_f$	L, S, L_N, S_N
e	$V_{rot} \gg \delta_f \gg V_e$	J, J_N

atom. The value of the ion–atom exchange interaction $\Delta(R_0)$ at this distance between the nuclei characterizes the character of moment coupling in the molecular ions at such separations.

Now, guided by the standard Hund scheme given in Table 7, we analyze the character of moment coupling in molecular ions. The standard scheme for a hierarchy of interaction energies in a diatomic molecule includes the Hund cases of moment coupling [2, 3, 12] and is based on three types of interaction: the electrostatic interaction potential V_{ex}, the fine level splitting or spin–orbital interaction δ_f, and the rotational energy V_{rot} due to relative motion of the nuclei in a diatomic molecule. There are six Hund cases of moment coupling depending on the relation between these interactions, and they are represented in Table 7.

The Table shows the quantum numbers of diatomic molecules in the framework of the Hund coupling scheme [2, 3, 12]. There, **L** is the total electron angular momentum of the molecule, **S** is the total electron spin, **J** is the total electron moment of the molecule, **n** is the unit vector along the molecular axis, **K** is the rotation moment of the nuclei, Λ is the projection of the angular momentum of electrons onto the molecular axis, Ω is the projection of the total electron moment **J** onto the molecular axis, S_n is the projection of the electron spin onto the molecular axis, and L_N, S_N, and J_N are projections of these moments onto the direction of the nucleus rotation momentum **N**. Below, we take this scheme as a basis for our analysis.

We now reduce the character of interaction inside molecular ions under consideration to the Hund scheme. We introduce the rotation energy in an ion–atom collision as

$$V_{rot} = \frac{\hbar v}{R_0}, \qquad (5.4)$$

where v is the relative ion–atom velocity and R_0 is the separation that determines the cross section of resonant charge exchange (5.3) for structureless cores. We compare the rotation energy V_{rot} with the exchange ion–atom interaction potential $\Delta(R_0)$ given by (5.3): their ratio is equal to

$$\frac{\Delta(R_0)}{V_{rot}(R_0)} = 0.28\sqrt{\frac{2}{\pi}}\sqrt{\gamma R_0} = 0.22\sqrt{\gamma R_0}. \qquad (5.5)$$

Because $\gamma R_0 \sim 10$ under thermal and eV-energies, it follows that the rotation energy and the exchange interaction potential are comparable for ion–atom distances that determine the cross section of resonant charge exchange. In addition, the rotation energy is small compared to other interaction potentials U_M, δ_i, and δ_a, and this determines the character of moment coupling in this case. Indeed, for the vanadium case with the d^3

electron shell, the distance between neighboring states with quantum numbers (4.1) or (4.2) is ~ 100 cm^{-1}, while $\Delta(R_0) \sim V_{rot} \sim 10$ cm^{-1}. We note that from the standpoint of the standard scheme of moment coupling given in Table 7, the conditions in Fig. 1 pertain to case "a" of Hund coupling, whereas Fig. 2 corresponds to case "c" of Hund coupling.

Based on the above analysis, we can construct a hierarchy of interactions for a quasimolecule consisting of an ion of the iron group of the periodical system of elements and its parent atom at typical distances R_0 between them that determine the cross section of resonant charge exchange in the range of collision energies 0.1–10 eV. As a result, we have the following hierarchy of interactions, which is more or less satisfied for all these cases:

$$V_{ex} \gg \delta_i, \delta_a \gg U \gg V_{rot}, \Delta(R_0). \tag{5.6}$$

Here, V_{ex} is a typical exchange interaction potential inside a separated atom and ion, which determines quantum numbers LS and ls for the atom and the ion, δ_i and δ_a are spin–orbit interactions in the atom and ion that lead to the quantum numbers J and j of the atom and the ion, and U is the interaction potential for the ion charge with the atom quadrupole moment. The hierarchy of interactions (5.6) is based on the data in Table 1 and the above analysis; it pertains to case "c" of Hund coupling.

We now analyze the above hierarchy of interactions for a molecular ion consisting of the identical ion and atom from the standpoint of the resonant charge exchange in collisions of ions and parent atoms with valence $3d$-electrons in ground states. In the notation of formula (4.2), the process of resonant charge exchange is accompanied by the following change of the ion and atom quantum numbers:

$$LSJM_Jlsjm_j \to LSJ'M'_Jlsj'm'_j. \tag{5.7}$$

Because the electron transfer proceeds at low rotation of the molecular axis, the transition of an s-electron leads to the following relations between momentum projections of the colliding atom and ion:

$$M'_J = M_J \pm 1/2, \quad m'_j = m_j \pm 1/2. \tag{5.8}$$

For an effective transfer of the s-electron, the resonance is required between the initial and final states with the accuracy of the ion–atom exchange interaction potential $\Delta(R)$ if this transition occurs at a separation R. $\Delta(R_0)$ is approximately 10 cm^{-1} according to the data in Table 6, where R_0 is determined by formula (5.3) and characterizes the cross section of resonant charge exchange for structureless cores. We see that $\Delta(R_0) < \Delta\varepsilon$, where $\Delta\varepsilon$ is the energy difference for neighboring energy levels with different J and j. Hence, the cross section of resonant charge exchange in collisions of ions and parent atoms with valence $3d$-electrons in ground states is less than the cross section in the case of structureless cores and the same parameters of the transferring s-electron. Evidently, the cross section of resonant charge exchange involving ions and atoms under consideration is given by the formula

$$\sigma_{res} = \frac{\pi R_1^2}{2}, \quad \Delta(R_1) \approx \Delta\varepsilon, \tag{5.9}$$

and according to Table 1, $\Delta\varepsilon = (20\text{–}40)$ cm^{-1} for $3d$-atoms and ions in the ground states. Hence, because $\Delta(R) \sim \exp(-\gamma)R$ according to formula (5.1), we have

$$R_0 - R_1 = (1-2)a_0. \tag{5.10}$$

This difference may be found more accurately for a certain case of electron transfer. As can be seen, even in the simple case of an s-electron transition, the charge exchange process requires taking some details of this process into account. In addition, the resonant charge exchange process pertains to the following hierarchy of interactions in the molecular ions instead of (5.6):

$$V_{ex} \gg \delta_i, \delta_a, U, \Delta(R_1) \gg V_{rot}. \tag{5.11}$$

Interaction hierarchy (5.6) corresponds to case "c" of Hund coupling, whereas (5.11) is related to the cases of Hund coupling intermediate between "a" and "c".

In considering the resonant charge exchange process that involves ions and parent atoms with valence $3d$-electrons, we obtain that this process proceeds effectively at separations where the coupling of the electron momenta due to spin–orbit interaction inside the colliding ion and atom is comparable to the exchange interaction potential due to transfer a $4s$-electron between atomic cores. This shows that the ion–atom exchange interaction becomes important for the moment coupling at small and moderate distances between the ion and the parent atom where this exchange interaction is comparable to the quadrupole ion–atom interaction. From this, it also follows that the scheme of moment coupling in molecular ions under consideration must be revised by accounting for the ion–atom exchange interaction at low separations, where the ion–atom quadrupole interaction exceeds the spin–orbit interaction inside the atom and ion.

6. CONCLUSION

As a result of the above analysis, we can construct a hierarchy of ion–atom interactions in a quasimolecule at large ion–atom separations R that determine the cross section of resonant charge exchange. In this case, atoms and ions contain valence $3d$-electrons, and resonant charge exchange results from transfer of a $4s$-electron, as is the case for most atoms and ions with not completed $3d$-shells in accordance with Table 1. At large separations, the hierarchy of interactions is given by formulas (5.6) and (5.11), according to which the interactions in the quasimolecule can be divided into three blocks. The strongest interaction is the exchange interaction inside an isolated atom and an ion, which involves electrons of the $3d$- and $4s$-electron shells. This interaction along with the structure of the electron shell for a given state gives the orbital moments and spins for the interacting atom and ion as the quantum numbers of these particles. In these cases, the quasimolecule quantum numbers for the ion and atom electron shells are $LSls$ (the orbital moment and spin of the atom and the same quantum numbers for the ion).

The second block of interactions includes the fine splitting of atom δ_a and ion δ_i levels, as well as the long-range charge–quadrupole interaction U between an ion and an atom. The charge–quadrupole interaction potential U may be arbitrary in comparison with the spin–orbit interaction inside the ion δ_i and atom δ_a depending on the ion–atom separation. The quantum numbers for these two blocks of interaction are JM_Jj or JMj (J and j are the total atom and ion moments and M and M_J are the projections of the atom orbital and total moments onto the quasimolecule axis) depending on the ion–atom separations.

The rotational energy V_{rot} is small compared with the above interactions, and we deal with cases "a" or "c" of Hund coupling according to Table 7. The ion-atom exchange interaction potential $\Delta(R)$ may be small or comparable with the spin–orbit and quadrupole interactions depending on the ion–atom separation R. The electron transition proceeds effectively where these interactions are comparable. We note that even in the simple case of the ground ion and atom states, where resonant charge exchange results from the transfer of an s-electron, the accurate evaluation of the cross section of this process becomes cumbersome.

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