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Dipole transition-matrix elements of the one-electron heterodiatomic quasimolecules

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The problem of dipole transition-matrix element calculation for optical transitions in multiply charged one-electron diatomic quasimolecules with unequal nuclear charges Z_1 and Z_2 has been stated and solved. The quasimolecule Z_1eZ_2 is a unique example of a two-center system for which the energy terms and dipole transition moments have been calculated precisely in the frame of a nonrelativistic approach. Particular examples for the optical transitions with $Z_1=1.5,2,2.5,3$ and $Z_2=1$ and with the principal quantum number of the united ion $n_u=1,2,3,4$ have been tabulated. The scaling rules make it possible to determine the matrix elements for quasimolecules having nuclear charge ratios such as 2:1, 3:1, 3:2, and 5:2. Zeros at intermediate R and zero limiting values at large R are the highlighted features of the matrix elements. The heteronucleus case generates a large number of asymptotically forbidden transitions corresponding to transitions of an electron from one ion to another.

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I. INTRODUCTION

The present work deals with the calculation of dipole transition-matrix elements and related optical values for transitions in multiply charged one-electron diatomic quasimolecules with unequal nuclear charges Z_1 and Z_2. (Hereafter we use the notation Z_1eZ_2 for such quasimolecules.) It is important to note that the results obtained will be used for subsequent spectral profile calculations of the optical transitions between quasimolecular states which correlate, at small internuclear distances, with the states of the united nucleus with principal quantum number $n_u=1,2,3,4$.

Up to now the most comprehensive calculations of the dipole transition-matrix elements for the case $Z_1=Z_2=1$ (hydrogen molecular ion H_2^+) have been performed by Ramaker and Peek [1] and motivated by problems arising in astrophysics. The data obtained have been applied successfully by Allard *et al.* [2] to the calculations of the spectral profiles produced by the atomic hydrogen Lyman-α and Lyman-β transitions broadened by collisions with ionized atomic hydrogen. The main conclusion of [2] is that the variation of the dipole has to be taken into account to obtain reliable results to be used as diagnostics of stellar and plasma parameters.

The first wave of interest in the spectral profiles produced by Z_1eZ_2 quasimolecules with different Z_1 and Z_2 was apparently induced by the observations of x-ray radiation under inner-shell excitation in ion-atom collisions. For a review of this field until 1984 see Anholt [3] and for some recent advances see, e.g., Schulze *et al.* [4]. Another wave came from hot dense plasma physics. At some density-temperature parameters of hot dense plasma, the excited-state orbitals of a bound electron (or bound electrons) are strongly disturbed by the field of the nearest-neighbor ion. Therefore, consideration of multiply charged quasimolecule ions makes physical sense. Within such an approach absorption and emission processes in hot dense plasmas are simply optical transitions in quasimolecules [5].

In terms of optical spectroscopy the phenomenon of quasimolecular radiation suggests two questions. First, what are the spectral profiles produced by such transitions? Second, what is the influence of configuration interactions in ion-atom collisions or in hot dense plasma conditions on spectral profiles? It seems reasonable to begin with the first question regarding the transitions produced by binary collisions of multicharged ions with only one bound electron. Such a method has been attempted previously in Ref. [6], where the spectral profiles produced by Lyman-α transitions were considered. Being aimed at a general description of the exchange interaction influence on the spectral profiles, the problem was considerably simplified in [6] with the assumptions of constant dipole matrix elements and exponential interaction energies. Such an approach works well for the description of spectral profiles that are connected to allowed transitions in an ion and produced by quasimolecular transitions, in the region of large internuclear distances. But the approach is totally improper for forbidden transitions marked by a strong dependence of the dipole matrix elements on the internuclear distance. Meanwhile an accurate computation of spectral profiles produced by the quasimolecules Z_1eZ_2 in the semiclassical approach (justified for collision energies of the order of several hundreds of eV) needs accurate values of dipole moments over a wide range of internuclear distances rather than being restricted to large ones only. In this context, preliminary computation [7] has revealed the occurrence of the roots of the dipole matrix elements at specific internuclear distances.

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To the best of the authors' knowledge, the dipole matrix elements for the quasimolecule Z_1eZ_2 with different Z_1 and Z_2 in the frame of a nonrelativistic approach have not been calculated, only the quasimolecular energy terms which have been reviewed in detail by Komarov *et al.* [8]. In the present paper we computed the dipole transition-matrix elements for one-electron diatomic quasimolecules with the nuclei charges $Z_1 > Z_2 = 1$. The matrix elements are calculated in a wide range of the internuclear distances R for the transitions coupling the lowest 16 electronic states. Particular attention is paid to the investigation of the roots of the dipole matrix elements. The corresponding oscillator strengths and probabilities of the radiative transitions can be immediately obtained from the computed matrix elements and the exact energy terms (see Sec. II).

The paper is organized as follows. In Sec. II we derive the formulas that relate the radiative characteristics of one-electron heterodiatomic quasimolecules. In Sec. III the method of calculation of the dipole moment matrix elements is described. Section IV deals with the results of calculations and their discussion. Finally, in Sec. V we give some conclusions and discuss some applications of the results to spectroscopy. The Appendix summarizes some formulas useful to check the results in two limiting cases, a united nucleus and separated nuclei. Atomic units $e = m = \hbar = 1$ are used throughout this work.

II. SCALING RELATIONS FOR THE RADIATIVE CHARACTERISTICS

The scaling relations between the characteristics of radiative transitions in hydrogenlike ions are well known. For instance, the probability of a radiative transition from state i to j for the hydrogenlike ion with nucleus charge Z can be expressed by means of the probability for the same transition in hydrogen, e.g., $W_{ij}(Z) = Z^4 W_{ij}(1)$ [9]. Below we shall derive the formulas that relate the radiative characteristics of the one-electron diatomic quasimolecule with nuclear charges Z_1 and Z_2 $(Z_1 \geqslant Z_2)$ to the same characteristics of the one-electron quasimolecule with nuclei charges $Z_1' = Z_1/Z_2$ and $Z_2' = 1$.

For an electron in the field of two fixed nuclei Z_1 and Z_2 separated at the distance R, the matrix element of the electric dipole moment operator between states specified by quantum numbers i, m_i and j, m_j is given by the following formula:

$$\vec{d}_{im_i,jm_j}(Z_1,Z_2,R) = \int \psi^*_{im_i}(\vec{r},R)\,\vec{r}\,\psi_{jm_j}(\vec{r},R)\,d\vec{r}. \qquad (1)$$

In Eq. (1) m_i and m_j stand for the magnetic quantum numbers, which determine the projection of the orbital momentum of the electron on the internuclear axis $\vec{R}$, $\vec{r}$ denotes the position vector of the electron, and ψ_{im_i} and ψ_{jm_j} are the two-Coulomb-center wave functions. These wave functions are solutions of the following Schrödinger equation:

$$\left(-\frac{1}{2}\Delta_{\vec{r}} - \frac{Z_1}{|\vec{r}+\vec{R}/2|} - \frac{Z_2}{|\vec{r}-\vec{R}/2|}\right)\psi_{im_i}(\vec{r},R) = \mathcal{E}_{i|m_i|}(R)\,\psi_{im_i}(\vec{r},R). \qquad (2)$$

$\Delta_{\vec{r}}$ is the Laplacian and $\mathcal{E}_{i|m_i|}(R)$ the energy term.

The oscillator strength $f_{ij}(Z_1, Z_2, R)$ corresponding to the electric dipole transition $i \rightarrow j$ is determined by means of the matrix element (1) [9], i.e.,

$$f_{ij}(Z_1,Z_2,R) = -\frac{2}{3}\frac{\varpi_{ij}(R)}{g_i}\sum_{m_i,m_j}|\vec{d}_{im_i,jm_j}(Z_1,Z_2,R)|^2, \qquad (3)$$

where $\varpi_{ij}(R) = \mathcal{E}_{i|m_i|}(R) - \mathcal{E}_{j|m_j|}(R)$ is the difference between the energy terms, and g_i is the degree of degeneracy or statistical weight of the initial level i ($g_i = 1$ for states with $m_i = 0$ and $g_i = 2$ for states with $m_i \neq 0$).

For spontaneous emission by a quasimolecule Z_1eZ_2 from the state i to j, the probability per time unit $A_{ij}(Z_1, Z_2, R)$ can be expressed in terms of the oscillator strength of the corresponding transition [9]:

$$A_{ij}(Z_1,Z_2,R) = 2\alpha^3\varpi^2_{ij}(R)|f_{ij}(Z_1,Z_2,R)|, \qquad (4)$$

where α is the fine structure constant ($\alpha = 1/137$).

Let us perform the following scale transformation:

$$\vec{r} = \vec{\rho}/Z_2, \quad \vec{R} = \vec{L}/Z_2; \qquad (5)$$

then Eq. (2) can be written as

$$\left(-\frac{1}{2}\Delta_{\vec{\rho}} - \frac{Z_1'}{|\vec{\rho}+\vec{L}/2|} - \frac{Z_2'}{|\vec{\rho}-\vec{L}/2|}\right)\varphi_{im_i}(\vec{\rho},L) = \varepsilon_{i|m_i|}(L)\,\varphi_{im_i}(\vec{\rho},L), \qquad (6)$$

where $Z_1' = Z_1/Z_2$, $Z_2' = 1$, and $\varepsilon_{i|m_i|}(L) = Z_2^{-2}\mathcal{E}_{i|m_i|}(L/Z_2)$.

It follows from the obtained formulas that the normalized eigenfunctions and eigenvalues of Eqs. (2) and (6) are connected by the relations [10]

$$\psi_{im_i}(\vec{r},R) = Z_2^{3/2}\varphi_{im_i}(Z_2\vec{r},Z_2R), \qquad (7)$$

$$\mathcal{E}_{i|m_i|}(R) = Z_2^2\varepsilon_{i|m_i|}(Z_2R). \qquad (8)$$

Substitution of Eq. (7) in Eq. (1) gives the relation between the matrix elements of the quasimolecules Z_1eZ_2 and $Z_1'eZ_2'$ [11]:

$$\vec{d}_{im_i,jm_j}(Z_1,Z_2,R) = \frac{1}{Z_2}\vec{d}_{im_i,jm_j}(Z_1',Z_2',L), \qquad (9)$$

where $\vec{d}_{im_i,jm_j}(Z_1',Z_2',L)$ is the matrix element of the electric dipole moment for the quasimolecule $Z_1'eZ_2'$.

Now, substituting Eqs. (8) and (9) in Eq. (3), one can write

$$f_{ij}(Z_1,Z_2,R) = f_{ij}(Z_1',Z_2',L), \qquad (10)$$

where $f_{ij}(Z_1', Z_2', L)$ is the oscillator strength of the dipole electric transition $i \rightarrow j$ for the quasimolecule $Z_1'eZ_2'$.

Thus, the oscillator strength of the quasimolecule Z_1eZ_2 does not change if we reduce the nuclear charges and increase the nuclear separation by the same factor Z_2 simultaneously. Next, applying Eq. (4), one can write

$$A_{ij}(Z_1,Z_2,R) = Z_2{}^4A_{ij}(Z_1',Z_2',L), \qquad (11)$$

where $A_{ij}(Z_1', Z_2', L)$ is the probability per time unit for the spontaneous emission taking place from state i to j.

In the particular case of homonuclear quasimolecules ($Z_1=Z_2=Z$), the radiative characteristics reduce to the ones relevant to the hydrogen molecular ion $H_2{}^+$:

$$\vec{d}_{im_i,jm_j}(Z,Z,R) = Z^{-1}\vec{d}_{im_i,jm_j}(1,1,ZR),$$

$$f_{ij}(Z,Z,R) = f_{ij}(1,1,ZR),$$

$$A_{ij}(Z,Z,R) = Z^4 A_{ij}(1,1,ZR). \tag{12}$$

Here $\vec{d}_{im_i,jm_j}(1,1,ZR)$, $f_{ij}(1,1,ZR)$, and $(A_{ij}1,1,ZR)$ stand for the matrix element of the electric dipole moment, the oscillator strength, and the transition probability for the molecule $H_2{}^+$, respectively.

The formulas obtained above reduce the calculation of the radiative characteristics of one-electron quasimolecules with the nuclear charges kZ_1 and kZ_2 ($k=1,2,3,\ldots$) to the calculation of the same characteristics for a single quasimolecule with the nuclear charges $Z_1'=Z_1/Z_2$ and $Z_2'=1$. We emphasize that the calculation of the radiative characteristics for quasimolecules with smaller nuclear charges is time saving and faced with smaller computational difficulties. It is also important to note that decreasing the nuclear charges increases the accuracy of the radiative characteristic computations.

III. CALCULATION OF THE DIPOLE MOMENT MATRIX ELEMENTS

It is well known that the Schrödinger equation (2) is separable by using the prolate spheroidal coordinate system (ξ,η,φ), e.g., [8], in which the x,y,z components of the electron position vector $\vec{r}$ can be written in terms of spherical coordinates as

$$x = \frac{R}{2}\sqrt{(\xi^2-1)(1-\eta^2)}\cos\varphi,$$

$$y = \frac{R}{2}\sqrt{(\xi^2-1)(1-\eta^2)}\sin\varphi, \tag{13}$$

$$z = \frac{R}{2}\xi\eta.$$

Then the solution of Eq. (2) can be presented as the following product:

$$\psi_{im_i}(\vec{r},R) = \frac{1}{\sqrt{2\pi}} X_{i|m_i|}(\xi,R) Y_{i|m_i|}(\eta,R) e^{im_i\varphi}, \tag{14}$$

$$1 \leqslant \xi < \infty, \quad -1 \leqslant \eta \leqslant 1, \quad 0 \leqslant \varphi < 2\pi.$$

Here $X_{i|m_i|}(\xi,R)$ and $Y_{i|m_i|}(\eta,R)$ stand for the two-Coulomb-center quasiradial and quasiangular wave functions, which are normalized according to

$$\frac{R^3}{8}\int_1^\infty \int_{-1}^1 X^2_{i|m_i|}(\xi,R) Y^2_{i|m_j|}(\eta,R)(\xi^2-\eta^2)\,d\xi\,d\eta = 1. \tag{15}$$

After integration over φ, the matrix elements [Eq. (1)] depending on the wave functions ψ_{im_i} and ψ_{jm_j} can be expressed through the forms

$$\begin{aligned}(d_x)_{im_i,jm_j} = \pm i(d_y)_{im_i,jm_j} = \frac{R^4}{32}\Bigg(&\int_1^\infty X_{i|m_i|}X_{j|m_j|}\sqrt{\xi^2-1}\,\xi^2 d\xi \\ &\times\int_{-1}^1 Y_{i|m_i|}Y_{j|m_j|}\sqrt{1-\eta^2}\,d\eta \\ &-\int_1^\infty X_{i|m_i|}X_{j|m_j|}\sqrt{\xi^2-1}\,d\xi \\ &\times\int_{-1}^1 Y_{i|m_i|}Y_{j|m_j|}\sqrt{1-\eta^2}\,\eta^2 d\eta\Bigg),\end{aligned} \tag{16}$$

$$\begin{aligned}(d_z)_{im_i,jm_j} = \frac{R^4}{16}\Bigg(&\int_1^\infty X_{i|m_i|}X_{j|m_j|}\xi^3 d\xi\int_{-1}^1 Y_{i|m_i|}Y_{j|m_j|}\eta\,d\eta \\ &-\int_1^\infty X_{i|m_i|}X_{j|m_j|}\xi\,d\xi\int_{-1}^1 Y_{i|m_i|}Y_{j|m_j|}\eta^3 d\eta\Bigg).\end{aligned} \tag{17}$$

They satisfy the selection rules for the magnetic quantum number in the case of dipole transitions, i.e., $m_j=m_i\mp 1$ in Eq. (16) for radiation polarized in the plane perpendicular to $\vec{R}$ (σ-π transitions) and $m_j=m_i$ in Eq. (17) for radiation polarized along the internuclear axis $\vec{R}$ (σ-σ and π-π transitions) [12]. For simplicity, in what follows, the sign of the magnetic quantum number is omitted.

The computational procedure implemented is as follows. First, we determine the separation constants for the equations and calculate the energy terms; then, we determine the wave functions of the quasimolecule Z_1eZ_2. In order to separate, from a great many energy terms, those corresponding to a given set of quantum numbers $\{i,m_i\}$, we find $\mathcal{E}_{im_i}(R)$ at $R \ll 1$, taking the value of this term at $R=0$ as the initial approximation. Further, increasing R by a ΔR step, we determine $\mathcal{E}_{im_i}(R)$ at larger R.

The wave functions $X_{\mathrm{im}_i}(\xi,R)$ and $Y_{im_i}(\eta,R)$ can be expanded in various forms [8]. For the quasiradial wave function, we use the well-known Jaffe expansion [13]

$$X_{\mathrm{im}_i}(\xi,R) = (\xi^2-1)^{m_i/2} e^{-P(\xi-1)}(\xi+1)^\sigma \sum_{s=0}^\infty a_s[(\xi-1)/(\xi+1)]^s, \tag{18}$$

where $P=R\sqrt{-\mathcal{E}_{im_i}(R)/2}$ and $\sigma=[R(Z_1+Z_2)/2P]-m_i-1$.

For the quasiangular wave function we take

$$Y_{\mathrm{im}_i}(\eta,R) = (1-\eta^2)^{m_i/2} e^{-P(1+\eta)}\sum_{s=0}^\infty b_s(1+\eta)^s \tag{19a}$$

and

TABLE I. Dipole moment matrix elements for transitions $2p\sigma\rightarrow 1s\sigma$ and $3d\sigma\rightarrow 1s\sigma$ in relation to the distance R between ions $Z_1=1.5$, 2.0, 2.5, 3.0 and $Z_2=1$; all values in atomic units.

	$2p\sigma\rightarrow 1s\sigma$				$3d\sigma\rightarrow 1s\sigma$			
R	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$
0.25	−0.33803	−0.28907	−0.25263	−0.22412	−0.00174	−0.00303	−0.00404	−0.00485
0.50	−0.41545	−0.36026	−0.31328	−0.27264	−0.00488	−0.00885	−0.01202	−0.01446
0.75	−0.50288	−0.42748	−0.35600	−0.29371	−0.01044	−0.01920	−0.02566	−0.02989
1.00	−0.58488	−0.47277	−0.36814	−0.28570	−0.01962	−0.03555	−0.04541	−0.05021
1.50	−0.70306	−0.48210	−0.32696	−0.23558	−0.05478	−0.08810	−0.09784	−0.09613
2.00	−0.73859	−0.41656	−0.26382	−0.19231	−0.12002	−0.15697	−.014965	−0.13021
2.50	−0.68315	−0.33383	−0.21462	−0.16807	−0.20965	−0.21854	−0.18207	−0.14208
3.00	−0.56969	−0.26313	−0.18281	−0.15913	−0.29820	−0.25760	−0.19418	−0.13747
3.50	−0.44511	−0.20898	−0.16470	−0.16077	−0.36338	−0.27608	−0.19380	−0.12248
4.00	−0.33529	−0.16811	−0.15710	−0.16779	−0.40070	−0.28197	−0.18663	−0.10089
4.50	−0.24687	−0.13647	−0.15830	−0.17481	−0.41596	−0.28172	−0.17467	−0.07747
5.00	−0.17850	−0.11095	−0.16738	−0.17913	−0.41672	−0.27920	−0.15713	−0.05717
6.00	−0.08884	−0.07110	−0.19803	−0.18181	−0.39782	−0.27401	−0.10127	−0.03076
7.00	−0.04175	−0.04202	−0.21427	−0.18187	−0.37434	−0.27132	−0.04739	−0.01693
8.00	−0.01880	−0.02280	−0.21733	−0.18147	−0.35788	−0.27062	−0.02052	−0.00928
9.00	−0.00821	−0.01163	−0.21755	−0.18103	−0.35023	−0.27079	−0.00893	−0.00494
10.0	−0.00352	−0.00570	−0.21727	−0.18062	−0.34912	−0.27106	−0.00390	−0.00255
12.0	−0.00062	−0.00127	−0.21655	−0.17992	−0.35424	−0.27107	−0.00074	−0.00063
14.0	−0.00010	−0.00026	−0.21591	−0.17938	−0.35822	−0.27060	−0.00014	−0.00014
16.0	−0.00002	−0.00005	−0.21537	−0.17896	−0.35959	−0.27004	−0.00002	−0.00003
18.0	0.00000	−0.00001	−0.21492	−0.17862	−0.35979	−0.26951	0.00000	−0.00001
20.0	0.00000	0.00000	−0.21455	−0.17834	−0.35957	−0.26904	0.00000	0.00000
22.0	0.00000	0.00000	−0.21423	−0.17810	−0.35922	−0.26862	0.00000	0.00000
24.0	0.00000	0.00000	−0.21397	−0.17790	−0.35883	−0.26825	0.00000	0.00000
26.0	0.00000	0.00000	−0.21373	−0.17773	−0.35844	−0.26793	0.00000	0.00000
28.0	0.00000	0.00000	−0.21353	−0.17759	−0.35807	−0.26764	0.00000	0.00000
30.0	0.00000	0.00000	−0.21336	−0.17746	−0.35773	−0.26739	0.00000	0.00000
∞	0.00000	0.00000	−0.21070	−0.17558	−0.35117	−0.26337	0.00000	0.00000

$$Y_{im_i}(\eta,R) = (1-\eta^2)^{m_i/2} e^{-P(1-\eta)} \sum_{s=0}^{\infty} b'_s (1-\eta)^s, \qquad (19b)$$

where Eqs. (19a) and (19b) are applied to the two η definite segments $[-1,0]$ and $[0,1]$, respectively.

The expansion coefficients a_s, b_s, and b'_s can be calculated from the three-term recurrence relations [8]. The recurrence relations leave the normalization uncertain. Therefore, the wave functions (19) have to be matched at the point $\eta=0$. As a consequence of accumulation of computational errors, the coefficients a_s increase monotonically starting from a specific s. Therefore, such coefficients should be dropped from the summation in Eq. (18) [8]. The procedure used yields a relative accuracy of order 10^{-12} for the energy terms and accuracy of order 10^{-8}–10^{-10} for the corresponding quasiradial and quasiangular wave functions. Thus, the accuracy of the calculated matrix elements can be estimated at 10^{-8}.

The signs of the dipole-strength matrix elements in Eqs. (16) and (17) depend on the phase convention for the involved wave functions. Our phase convention generates a sign that coincides with the sign of the same matrix element calculated with parabolic wave functions [14] in the limit of separated nuclei (see the Appendix).

IV. RESULTS AND DISCUSSION

With the algorithm described in Sec. III we have calculated the dipole matrix elements for all transitions between the states with principal quantum number in the united ion limit $n_u=1,2,3$, and for four transitions involving $n_u=4$. The calculations have been carried out for quasimolecules with the nuclear charges $Z_1=1.5,2,2.5,3$ and $Z_2=1$. It should be noted that noninteger values of nuclear charges might be studied with the same algorithm. For example, they naturally fit the description of screened Coulomb molecular orbitals [15]. The calculated matrix elements for the transitions cou-

TABLE II. Dipole moment matrix elements for transitions $3d\sigma \rightarrow 1s\sigma$ and $4f\pi \rightarrow 1s\sigma$ in relation to the distance R between ions $Z_1=1.5$, 2.0, 2.5, 3.0 and $Z_2=1$; all values in atomic units.

	$3d\sigma \rightarrow 1s\sigma$				$4f\pi \rightarrow 1s\sigma$			
R	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$
0.25	0.00106	0.00184	0.00245	0.00293	0.00003	0.00004	0.00005	0.00006
0.50	0.00292	0.00525	0.00706	0.00840	0.00015	0.00020	0.00025	0.00030
0.75	0.00608	0.01098	0.01437	0.01635	0.00041	0.00056	0.00070	0.00084
1.00	0.01105	0.01939	0.02387	0.02534	0.00089	0.00120	0.00148	0.00171
1.50	0.02825	0.04242	0.04380	0.04037	0.00281	0.00357	0.00405	0.00437
2.00	0.05575	0.06595	0.05785	0.04808	0.00639	0.00737	0.00780	0.00797
2.50	0.08848	0.08269	0.06438	0.05007	0.01172	0.01237	0.01237	0.01204
3.00	0.11794	0.09134	0.06548	0.04912	0.01851	0.01821	0.01727	0.01599
3.50	0.13901	0.09356	0.06358	0.04718	0.02638	0.02446	0.02199	0.01932
4.00	0.15109	0.09151	0.06050	0.04528	0.03495	0.03062	0.02606	0.02172
4.50	0.15556	0.08709	0.05731	0.04385	0.04379	0.03624	0.02922	0.02315
5.00	0.15421	0.08170	0.05455	0.04297	0.05244	0.04103	0.03139	0.02369
6.00	0.14034	0.07121	0.05101	0.04257	0.06767	0.04766	0.03298	0.02280
7.00	0.11981	0.06338	0.04991	0.04315	0.07876	0.05062	0.03173	0.02055
8.00	0.09921	0.05869	0.05039	0.04393	0.08559	0.05077	0.02867	0.01822
9.00	0.08153	0.05677	0.05150	0.04459	0.08906	0.04517	0.02486	0.01647
10.0	0.06731	0.05710	0.05259	0.04511	0.09025	0.03380	0.02123	0.01550
12.0	0.04695	0.06158	0.05407	0.04585	0.08948	0.02146	0.01614	0.01567
14.0	0.03288	0.06578	0.05492	0.04637	0.08813	0.01277	0.01399	0.01731
16.0	0.02189	0.06780	0.05550	0.04676	0.08779	0.00747	0.01427	0.01858
18.0	0.01334	0.06879	0.05594	0.04707	0.08839	0.00426	0.01708	0.01925
20.0	0.00747	0.06941	0.05629	0.04732	0.08944	0.00234	0.02102	0.01965
22.0	0.00394	0.06988	0.05657	0.04753	0.09057	0.00124	0.02286	0.01995
24.0	0.00200	0.07025	0.05682	0.04771	0.09154	0.00064	0.02351	0.02018
26.0	0.00098	0.07057	0.05702	0.04786	0.09230	0.00032	0.02387	0.02038
28.0	0.00047	0.07084	0.05720	0.04798	0.09289	0.00016	0.02413	0.02054
30.0	0.00022	0.07107	0.05736	0.04810	0.09336	0.00000	0.02435	0.02069
∞	0.00000	0.07458	0.05966	0.04972	0.09944	0.00000	0.02043	0.01703

pling the ground state and the excited states are presented in Tables I–V with only two matrix elements for the transitions involving the $n_u=4$ states. Table VI gives examples for transitions between $n_u=4$ and excited states.

The most prominent features, which can be deduced from the tabulated data, are as follows. (i) The matrix elements strongly depend on the internuclear distance R. (ii) Some matrix elements of the quasimolecules, with different Z_1 at large R, exchange their limiting values. (iii) The limiting values of some matrix elements, at large R, tend in pairs to the same values or to values of equal moduli and opposite signs, and some of them are equal to zero. (iv) Some of the matrix elements have zeros at intermediate R. Below, some features are discussed qualitatively in more detail.

A. Limiting values

The coincidence of some limiting values could already be found from the results obtained in [1] for one-electron homonuclear quasimolecules and checked using the formulas for the matrix elements of the hydrogen atom in parabolic coordinates (see the Appendix), and the *g*-*u* symmetry of the wave functions. A different feature for heteronuclear quasimolecules is that the correlation diagram, which relates the orbitals of the isolated and united ions, now depends on Z_1. Such dependence has been used in the physics of inner-shell collision excitation [16]. More precisely, the rearrangement for the dipole matrix elements of the molecular orbital (MO) correlation diagrams results in the dependence of the limiting values on Z_1, apart from a trivial scaling, and in the exchange of the limiting values.

The MO correlation diagrams can be constructed with the rules obtained in Refs. [15,17]. But with the aim of spectroscopic applications, Figs. 1–3 epict the real MO energy diagrams. These MO energy diagrams have been calculated with the procedure described in Sec. III for quasimolecules with $Z_1=1.5, 2, 2.5$. There is a one-to-one correspondence between the united ion and the separated ion states for the

TABLE III. Dipole moment matrix elements for transitions $2s\sigma \rightarrow 1s\sigma$ and $3s\sigma \rightarrow 1s\sigma$ in relation to the distance R between ions $Z_1=1.5$, 2.0, 2.5, 3.0 and $Z_2=1$; all values in atomic units.

	$2s\sigma \rightarrow 1s\sigma$				$3s\sigma \rightarrow 1s\sigma$			
R	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$
0.25	0.00998	0.01681	0.02173	0.02536	0.00434	0.00731	0.00944	0.01101
0.50	0.02243	0.03784	0.04819	0.05470	0.00971	0.01634	0.02077	0.02354
0.75	0.03795	0.06288	0.07688	0.08289	0.01631	0.02694	0.03289	0.03546
1.00	0.05674	0.09032	0.10393	0.10555	0.02419	0.03843	0.04427	0.04506
1.50	0.10344	0.14291	0.14352	0.13277	0.04343	0.06040	0.06112	0.05680
2.00	0.15701	0.180998	0.16492	0.14568	0.06531	0.07659	0.07047	0.06244
2.50	0.20654	0.20391	0.17642	0.15261	0.08571	0.08665	0.07555	0.06539
3.00	0.24396	0.21747	0.18327	0.15686	0.10150	0.09274	0.07851	0.06708
3.50	0.26911	0.22600	0.18775	0.15973	0.11249	0.09659	0.08036	0.06812
4.00	0.28560	0.23177	0.19092	0.16181	0.11996	0.09914	0.08158	0.06880
4.50	0.29672	0.23592	0.19328	0.16338	0.12516	0.10090	0.08241	0.06925
5.00	0.30456	0.23905	0.19510	0.16461	0.12890	0.10216	0.08299	0.06957
6.00	0.31476	0.24346	.19775	0.16644	0.13379	0.10377	0.08370	0.06995
7.00	0.32107	0.24642	0.19960	0.16772	0.13669	0.10467	0.08409	0.07015
8.00	0.32537	0.24857	0.20096	0.16868	0.13850	0.10520	0.08431	0.07026
9.00	0.32848	0.25020	0.20202	0.16943	0.13966	0.10552	0.08443	0.07032
10.0	0.33086	0.25149	0.20286	0.17003	0.14042	0.10571	0.08450	0.07036
12.0	0.33427	0.25340	0.20412	0.17093	0.14125	0.10589	0.08456	0.07039
14.0	0.33662	0.25477	0.20503	0.17157	0.14161	0.10594	0.08457	0.07039
16.0	0.33835	0.25579	0.20571	0.17206	0.14174	0.10593	0.08456	0.07039
18.0	0.33969	0.25659	0.20624	0.17244	0.14176	0.10591	0.08455	0.07038
20.0	0.34077	0.25724	0.20667	0.17275	0.14173	0.10588	0.08453	0.07038
22.0	0.34165	0.25777	0.207703	0.17300	0.14168	0.10584	0.08452	0.07037
24.0	0.34239	0.25821	0.20732	0.17321	0.14161	0.10581	0.08450	0.07037
26.0	0.34302	0.25859	0.20757	0.17339	0.14155	0.10578	0.08449	0.07036
28.0	0.34356	0.25892	0.20779	0.17354	0.14148	0.10575	0.08448	0.07036
30.0	0.34403	0.25919	0.20798	0.17367	0.14142	0.10573	0.08447	0.07035
∞	0.35117	0.26337	0.21070	0.17558	0.14063	0.10547	0.08438	0.07031

case of $Z_1=3$, $Z_2=1$ and the case $Z_1=2.5$, $Z_2=1$.

To exemplify the dependence of the limiting values on Z_1 we take the particular case of the matrix element, i.e., $\langle 010|d_z|000\rangle = -128/243Z_1$, for the hydrogenlike ion [see Eq. (A5)]. According to Figs. 1–3 this matrix element is the limiting value for the transition between the $3d\sigma$ and $1s\sigma$ states in the case of $Z_1=1.5,2$, but in the case $Z_1=2.5,3$, this matrix element is the limiting value for the transition between the $2p\sigma$ and $1s\sigma$ states see (Table I). Another example is the matrix element $\langle 011|d_x|000\rangle = 27\sqrt{2}/256Z_1$. Indeed, Figs. 1 and 2 demonstrate that this matrix element is the limiting value for the transitions between the $4f\pi$ and $1s\sigma$ MO states in the case of $Z_1=1.5$, but in the case of $Z_1=2,2.5,3$ this matrix element is the limiting value for the transition between the $3d\pi$ and $1s\sigma$ states (see Table II). Figures 1–3 show that the $2s\sigma$, $2p\pi$, $3s\sigma$, and $3p\pi$ MO energy diagrams do not depend on Z_1 and their limiting values are determined by Eqs. (A5) and (A7).

The equality of the limiting values at $R \rightarrow \infty$ may also be explained in terms of matrix elements for hydrogenlike ions, calculated in parabolic coordinates. For instance, the result $\langle 010|d_z|000\rangle = -\langle 100|d_z|000\rangle$ [Eq. (A4)] leads to the equality of the matrix elements $\langle 2p\sigma|d_z|1s\sigma\rangle = -\langle 2s\sigma|d_z|1s\sigma\rangle$ for $Z_1=2.5,3$ and $\langle 3d\sigma|d_z|1s\sigma\rangle = -\langle 2s\sigma|d_z|1s\sigma\rangle$ for $Z_1=1.5,2$ at $R \rightarrow \infty$ (see also Tables I and III). In a similar way, the result $\langle 011|d_x|000\rangle = \langle 101|d_x|000\rangle$ [Eq. (A6)] will lead to the equality of the limiting values for the matrix elements $\langle 3d\pi|d_x|1s\sigma\rangle = \langle 3p\pi|d_x|1s\sigma\rangle$ in the case $Z_1=2$, 2.5, 3, and for the matrix elements $\langle 4f\pi|d_x|1s\sigma\rangle = \langle 3p\pi|d_x|1s\sigma\rangle$ in the case $Z_1=1.5$ at $R \rightarrow \infty$ (see also Tables II and IV).

B. Asymptotically forbidden transitions

When the dipole matrix element between two states of an atom or an ion is equal to zero, the transition is forbidden. Nevertheless, interaction between particles during collisions will allow the dipole matrix elements to become functions of internuclear distance and optical transitions to be allowed. Such optical transitions can be identified as true quasimo-

TABLE IV. Dipole moment matrix elements for transitions $2p\pi \rightarrow 1s\sigma$ and $3p\pi \rightarrow 1s\sigma$ in relation to the distance R between ions $Z_1=1.5$, 2.0, 2.5, 3.0 and $Z_2=1$; all values in atomic units.

	$2p\pi \rightarrow 1s\sigma$				$3p\pi \rightarrow 1s\sigma$			
R	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$
0.25	0.23158	0.19653	0.17077	0.15091	0.08968	0.07559	0.06534	0.05751
0.50	0.26521	0.22664	0.19633	0.17182	0.09746	0.08243	0.07107	0.06215
0.75	0.29803	0.25228	0.21432	0.18332	0.10429	0.08767	0.07472	0.06445
1.00	0.32704	0.27084	0.22374	0.18692	0.10984	0.09121	0.07649	0.06501
1.50	0.36996	0.28661	0.22541	0.18400	0.11741	0.09392	0.07645	0.06388
2.00	0.39011	0.28375	0.21981	0.17988	0.12058	0.09298	0.07482	0.06231
2.50	0.38990	0.27591	0.21528	0.17761	0.11994	0.09101	0.07328	0.06102
3.00	0.37859	0.26950	0.21281	0.17660	0.11718	0.08925	0.07209	0.05999
3.50	0.36544	0.26564	0.21169	0.17618	0.11408	0.08796	0.07117	0.05915
4.00	0.35495	0.06375	0.21124	0.17599	0.11151	0.08704	0.07042	0.05843
4.50	0.34806	0.26303	0.21106	0.17589	0.10966	0.08639	0.06979	0.05781
5.00	0.34434	0.26289	0.21100	0.17583	0.10845	0.08590	0.06923	0.05726
6.00	0.34306	0.26314	0.21094	0.17575	0.10743	0.08517	0.06827	0.05634
7.00	0.34524	0.26338	0.21089	0.17570	0.10750	0.08457	0.06746	0.05561
8.00	0.34762	0.26349	0.21085	0.17567	0.10799	0.08399	0.06676	0.05501
9.00	0.34926	0.26380	0.21082	0.17565	0.10852	0.08344	0.06617	0.05452
10.0	0.35021	0.26353	0.21080	0.17563	0.10890	0.08291	0.06566	0.05410
12.0	0.35099	0.26350	0.21076	0.17561	0.10910	0.08197	0.06483	0.05346
14.0	0.35121	0.26347	0.21074	0.17560	0.10881	0.08118	0.06419	0.05297
16.0	0.35126	0.26345	0.21073	0.17560	0.10832	0.08052	0.06369	0.05260
18.0	0.35127	0.26343	0.21072	0.17559	0.10777	0.07997	0.06329	0.05230
20.0	0.35126	0.26342	0.21072	0.17559	0.10724	0.07951	0.06296	0.05206
22.0	0.35125	0.26341	0.21071	0.17559	0.10674	0.07912	0.06268	0.05186
24.0	0.35124	0.26340	0.21071	0.17559	0.10629	0.07878	0.06245	0.05169
26.0	0.35123	0.26340	0.21071	0.17559	0.10588	0.07849	0.06224	0.05154
28.0	0.35122	0.26339	0.21071	0.17559	0.10551	0.07824	0.06207	0.05142
30.0	0.35121	0.26339	0.21071	0.17559	0.10518	0.07801	0.06192	0.05131
∞	0.35117	0.26337	0.21070	0.17558	0.09944	0.07458	0.05966	0.04972

lecular ones, and up to now some of these transitions produced in atomic and ionic collisions have been studied; see e.g., [18].

In their work on the H_2^+ dipole matrix elements, Ramaker and Peek [1(a)] have pointed out five asymptotically forbidden transitions with $\Delta m=0$. It is obvious that heteronuclear quasimolecules also have the same asymptotically forbidden transitions corresponding to transitions for isolated ions. For example, the transition $\langle 3p\sigma | d_z | 1s\sigma \rangle$ for $Z_1=2,2.5,3$ (see Table V), the dipole moment of which tends to the transition moment $\langle 110 | d_z | 000 \rangle$ when increasing R, is consequently equal to zero when $R \rightarrow \infty$ [Eq. (A4)]. It can be said that such transitions are induced by the perturbation of a bound electron by an external ion.

In heteronuclear quasimolecules there is an additional possibility for asymptotically forbidden transitions. When at $R \rightarrow \infty$ the upper and lower states belong to different ions, the corresponding wave functions do not overlap and therefore the matrix element is equal to zero. At smaller R, the interaction between two different ions will allow optical transitions corresponding to the transition of one electron from one ion to the other. Examples of such transitions are discussed below.

The prominent distinction of heteronuclear quasimolecules is the transformation of the strongest transition-matrix elements, connecting the resonance charge exchange states of the homonuclear quasimolecules, into matrix elements of forbidden transitions. According to Mulliken [19] for the homonuclear case, the dipole moments of the resonance charge transfer transitions are proportional to $R/2$ at large R. In the heteronuclear case, such optical transitions accompany nonresonant charge exchange, leading to the electron transition from one ion to another at large R. Therefore, such transitions correspond to asymptotically forbidden ones. As examples the transitions $2p\sigma$-$1s\sigma$ for $Z_1=1.5,2$ and $3d\sigma$-$1s\sigma$ for $Z_1=2.5,3$ accompanying the charge exchange between the lowest ion states with parabolic sets (000) and (000)′ correspond to such asymptotically forbidden transitions (see Table I).

TABLE V. Dipole moment matrix elements for transitions $3p\sigma \rightarrow 1s\sigma$ and $4p\sigma \rightarrow 1s\sigma$ in relation to the distance R between ions $Z_1=1.5$, 2.0, 2.5, 3.0 and $Z_2=1$; all values in atomic units.

	$3p\sigma \rightarrow 1s\sigma$				$4p\sigma \rightarrow 1s\sigma$			
R	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$
0.25	−0.12796	−0.10778	−0.09289	−0.08137	−0.07421	−0.06223	−0.05341	−0.04662
0.50	−0.13743	−0.11347	−0.09481	−0.08004	−0.07673	−0.06251	−0.05167	−0.04327
0.75	−0.13436	−0.10445	−0.08230	−0.06729	−0.07096	−0.05396	−0.04225	−0.03417
1.00	−0.11617	−0.08495	−0.06615	−0.05399	−0.05717	−0.04080	−0.03165	−0.02597
1.50	−0.06109	−0.04839	−0.04293	−0.03791	−0.02412	−0.01944	−0.01814	−0.01653
2.00	−0.01617	−0.02939	−0.03216	−0.03033	−0.00027	−0.00881	−0.01182	−0.01179
2.50	0.00886	−0.02113	−0.02680	−0.02630	0.01284	−0.00385	−0.00833	−0.00881
3.00	0.01882	−0.01735	−0.02389	−0.02393	0.01881	−0.00122	−0.00606	−0.00665
3.50	0.02062	−0.01549	−0.02229	−0.02235	0.02099	0.00036	−0.00442	−0.00494
4.00	0.01898	−0.01459	−0.02142	−0.02111	0.02138	0.00139	−0.00313	−0.00352
4.50	0.01626	−0.01426	−0.02095	−0.02001	0.02096	0.00211	−0.00207	−0.00231
5.00	0.01345	−0.01431	−0.02062	−0.01897	0.02016	0.00264	−0.00114	−0.00126
6.00	0.00871	−0.01520	−0.01989	−0.01705	0.01817	0.00340	0.00044	0.00047
7.00	0.00537	−0.01666	−0.01885	−0.01537	0.01619	0.00403	0.00177	0.00182
8.00	0.00313	−0.01808	−0.01766	−0.01394	0.01447	0.00465	0.00290	0.00290
9.00	0.00169	−0.01888	−0.01646	−0.01273	0.01306	0.00529	0.00386	0.00378
10.0	0.00080	−0.01894	−0.01536	−0.01171	0.01197	0.00593	0.00469	0.00452
12.0	0.00004	−0.01787	−0.01346	−0.01007	0.01060	0.00714	0.00604	0.00568
14.0	−0.00010	−0.01641	−0.01194	−0.00882	0.01021	0.00821	0.00709	0.00656
16.0	−0.00008	−0.01504	−0.01072	−0.00785	0.01082	0.00913	0.00793	0.00725
18.0	−0.00005	−0.01383	−0.00971	−0.00707	0.01228	0.00993	0.00862	0.00781
20.0	−0.00002	−0.01277	−0.00887	−0.00643	0.01367	0.01061	0.00919	0.00826
22.0	−0.00001	−0.01186	−0.00817	−0.00589	0.01448	0.01120	0.00968	0.00865
24.0	−0.00001	−0.01106	−0.00756	−0.00544	0.01504	0.01172	0.01010	0.00897
26.0	0.00000	−0.01036	−0.00704	−0.00505	0.01552	0.01219	0.01046	0.00926
28.0	0.00000	−0.00973	−0.00659	−0.00471	0.01596	0.01260	0.01078	0.00950
30.0	0.00000	−0.00918	−0.00619	−0.00442	0.01637	0.01296	0.01107	0.00972
∞	0.00000	0.00000	0.00000	0.00000	0.02621	0.01966	0.01573	0.01311

In homonuclear quasimolecules, only one of the two excited states that are involved in the resonant charge exchange is tied up by an optical transition to the $1s\sigma_g$ ground state. In the heteronuclear case, each of the excited states is tied up by an optical transition with the ground state. In the heteronuclear case, the states that are the u excited states in the homonuclear case belong, for large interionic distances, to the ion Z_2, in the case of a sufficiently small difference between Z_1 and Z_2 and of small n_u. As a consequence, the states under discussion have the zero value limit at large R for transition-matrix elements for transitions to the ground state. Of even greater importance for spectroscopy is the fact that, at intermediate R, the parallel transitions, forbidden in the homonuclear case due to parity violation and allowed in the heteronuclear case, are the strongest now. For example, in the $Z_1=1.5$ case, the strong $3p\sigma_u$-$1s\sigma_g$ transition gives rise to the asymptotically forbidden $3p\sigma$-$1s\sigma$ transition, while the forbidden $2s\sigma_g$-$1s\sigma_g$ transition gives rise to the $2s\sigma$-$1s\sigma$ transition, $2s\sigma$-$1s\sigma$ being the dominant transition (see Tables III and V). In the case of perpendicular transitions involving π excited states, the transitions forbidden for all R due to the parity violations are forbidden at large R in the heteronuclear case for sufficiently small difference between Z_1 and Z_2, e.g., the $3d\pi$-$1s\sigma$, $2p\pi$-$1s\sigma$ transitions for $Z_1=1.5$ (see Tables II and IV).

C. Zeros in the dipole transition moments

The properties of the dipole transition-matrix elements discussed above could be predicted, in principle, before any calculation by examining the correlation diagrams. This is not the case for zeros in the dipole moments. Up to now there are no rules that help to predict them reliably.

The existence of zeros in the dipole transition-matrix elements has already been pointed out for symmetrical quasimolecules. For instance, Ramaker and Peek [1] considered the lowest 20 electronic states of H_2^+ and found 14 matrix elements with zeros. In the heteronuclear case parallel tran-

TABLE VI. Dipole moment matrix elements for transitions $4f\sigma \rightarrow 2p\sigma$ and $4f\pi \rightarrow 2p\sigma$ in relation to the distance R between ions $Z_1=1.5$, 2.0, 2.5, 3.0 and $Z_2=1$; all values in atomic units.

	$4f\sigma \rightarrow 2p\sigma$				$4f\pi \rightarrow 2p\sigma$			
R	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$	$Z_1=1.5$	$Z_1=2.0$	$Z_1=2.5$	$Z_1=3.0$
0.25	−0.00237	−0.00390	0.00404	−0.00569	0.00137	0.00225	0.00285	0.00328
0.50	−0.00422	−0.00670	0.00825	−0.00929	0.00243	0.00385	0.00473	0.00532
0.75	−0.00529	−0.00813	0.00994	−0.01136	0.00303	0.00464	0.00565	0.00642
1.00	−0.00570	−0.00871	−0.01100	−0.01328	0.00324	0.00491	0.00614	0.00735
1.50	−0.00529	−0.00857	−0.01280	−0.01886	0.00291	0.00459	0.00670	0.00967
2.00	−0.00268	−0.00579	−0.01419	−0.02951	0.00127	0.00258	0.00640	0.01330
2.50	0.00459	−0.00199	−0.01534	−0.05223	−0.00292	−0.00236	0.00487	0.02013
3.00	0.01957	0.01785	−0.01801	−0.10027	−0.01098	−0.01156	0.00226	0.03378
3.50	0.04538	0.04559	−0.02695	−0.18828	−0.02387	−0.02633	−0.00025	0.05844
4.00	0.08494	0.08889	−0.05125	−0.31379	−0.04206	−0.04781	0.00000	0.09401
4.50	0.13993	0.14923	−0.10431	−0.44552	−0.06536	−0.07664	0.00779	0.13157
5.00	0.20882	0.22424	−0.20154	−0.54908	−0.09279	−0.11274	0.03001	0.16009
6.00	0.36267	0.39407	−0.52280	−0.64785	−0.15318	−0.20117	0.12847	0.18030
7.00	0.48942	0.53906	−0.75322	−0.66072	−0.20900	−0.29326	0.21165	0.17037
8.00	0.56566	0.61320	−0.79977	−0.64672	−0.25166	−0.36920	0.22596	0.05220
9.00	0.59768	0.61511	−0.77908	−0.63290	−0.27927	−0.42357	0.20658	0.13662
10.0	0.59865	0.57147	−0.75186	−0.62644	−0.29327	−0.46041	0.17871	0.12700
12.0	0.55419	0.44099	−0.73305	−0.62611	−0.28910	−0.49827	0.13420	0.12499
14.0	0.50122	0.31285	−0.74178	−0.62686	−0.25327	−0.50396	0.11352	0.13511
16.0	0.46830	0.19631	−0.74832	−0.62592	−0.19714	−0.50199	0.11302	0.14277
18.0	0.45910	0.10147	−0.74984	−0.62445	−0.13581	−0.50511	0.13264	0.14619
20.0	0.46871	0.04407	−0.74932	−0.62295	−0.08411	−0.51140	0.16091	0.14793
22.0	0.48823	0.01730	−0.74819	−0.62158	−0.04805	−0.51707	0.17334	0.14905
24.0	0.50731	0.00643	−0.74692	−0.62036	−0.02588	−0.52085	0.17692	0.14989
26.0	0.52012	0.00230	−0.74568	−0.61928	−0.01335	−0.52307	0.17849	0.15055
28.0	0.52703	0.00080	−0.74452	−0.61833	−0.00667	−0.52436	0.17951	0.15111
30.0	0.53047	0.00027	−0.74346	−0.61748	−0.00324	−0.52513	0.18029	0.15157
∞	0.52675	0.00000	−0.72548	−0.60457	0.00000	−0.52675	0.18923	0.15769

sitions having zeros in the symmetrical case have zeros for all Z_1 values considered here, namely, $4p\sigma$-$1s\sigma$ $(5U,1G)$ (see Table V), $4d\pi$-$2p\pi$ $(8G,4U)$, $4d\sigma$-$2p\sigma$ $(8G,4U)$. The matrix element for the transition $3p\sigma$-$1s\sigma$ $(2U,1G)$ has two zeros but only for $Z_1=1.5$ and has no zero otherwise (see Table V) (the notations in parentheses indicate the proper transitions for the symmetrical case according to [1]). The surprising result is a zero for the transition $3s\sigma$-$2p\sigma$ while this is not the case for the proper transition $(5G,1U)$ in homonuclear quasimolecules.

Similarly, there are zeros for all Z_1 for the perpendicular transitions $3s\sigma$-$2p\pi$ $(5G,4U)$, $4d\sigma$-$2p\pi$ $(6G,4U)$. In the cases of transitions $3p\pi$-$2p\sigma$, $4d\sigma$-$2s\sigma$, $4d\pi$-$2s\sigma$, $4p\pi$-$2s\sigma$, there are roots for all Z_1 although the proper transitions are forbidden in the symmetrical case due to parity violation. Finally, the matrix elements for the transitions $4s\sigma$-$2p\sigma$ and $4s\sigma$-$2p\pi$ have zeros, but the proper transitions have not been analyzed in the homonuclear case [1].

Inspecting the results of calculations for H_2^+ Lewis, McDowell, and Moiseiwitsch [20] noted that the quasiradial wave function of the upper state in each of the matrix elements with zero has at least one node. This condition is satisfied for the transitions in the heteronuclear quasimolecules under consideration above. The qualitative discussion of the condition for the existence of zeros in the heteronuclear case can be found in [21].

Finally, let us consider the transitions $4f\sigma$-$2p\sigma$ and $4f\pi$-$2p\sigma$. They are forbidden due to parity violation in the homonuclear case and have no nodes in the quasiradial wave functions of the upper and lower states. Nevertheless, both of them have zeros in the heteronuclear cases $Z_1=1.5,2$ (Table VI). At larger Z_1 both transitions can be described qualitatively as transitions between two excited states of the heavier ion in the field of the lighter ion (see Figs. 1–3).

V. CONCLUSIONS

The dipole matrix elements for the optical transitions σ-σ, σ-π, π-π in heteronuclear quasimolecules Z_1eZ_2 with

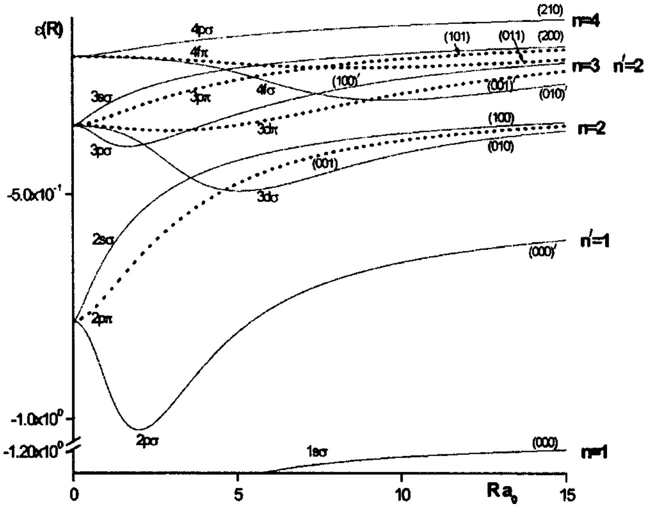

FIG. 1. Molecular orbital correlation diagram for the quasimolecule $Z_{1e}Z_2$ with $Z_1=1.5$ and $Z_2=1$. For the notation of the molecular orbitals we use the united ion designation in the left part of the figure and parabolic quantum numbers in brackets in the right part of the figure. n stands for the main quantum number in the separated-ion limit, and the primed numbers are for the ion with $Z_1=1$.

$Z_1=1.5,2,2.5,3$, $Z_2=1$, and $n_u=1,2,3,4$ have been calculated. The scaling relation makes it possible to determine the matrix elements for "one-electron quasi-molecules" having nuclear charge ratios such as 2:1, 3:1, 3:2, 5:2. The results obtained are very accurate but they do not include relativistic effects. Joined to those for the quasimolecule H_2^+, they give reliable input data for spectral line profile calculations in inner-shell collision physics and hot dense plasma physics.

Zeros at intermediate R and zero limiting values at large R are the highlighted features of the matrix elements. Although such features have been observed for the H_2^+ quasimolecule earlier, the heteronuclear case exhibits some additional features. It has been found that, in contrast to homonuclear quasimolecules, zeros may exist even for nodeless quasiradial functions for both states involved. Furthermore, the heteronuclear case generates a large number of asymptotically forbidden transitions corresponding to transitions of one electron from one ion to another. This latter feature has not been reported up to now to our knowledge, although it could be found in nonsymmetrical collisions of heavy rare-gas atoms or heavy alkali-metal atoms. Moreover, the approximation of a constant dipole matrix element in the spectral wing calculations is generally less justified for heteronuclear quasimolecules than for homonuclear ones.

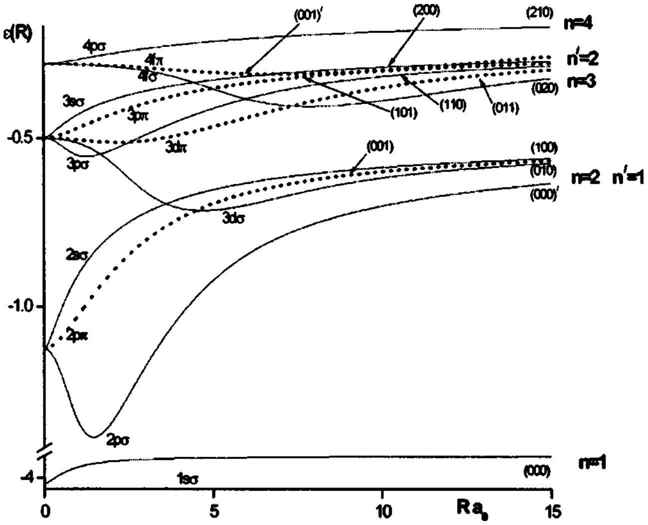

FIG. 2. Molecular orbital correlation diagram for the quasimolecule $Z_{1e}Z_2$ with $Z_1=2.0$ and $Z_2=1$. The notations are similar to the ones on Fig. 1.

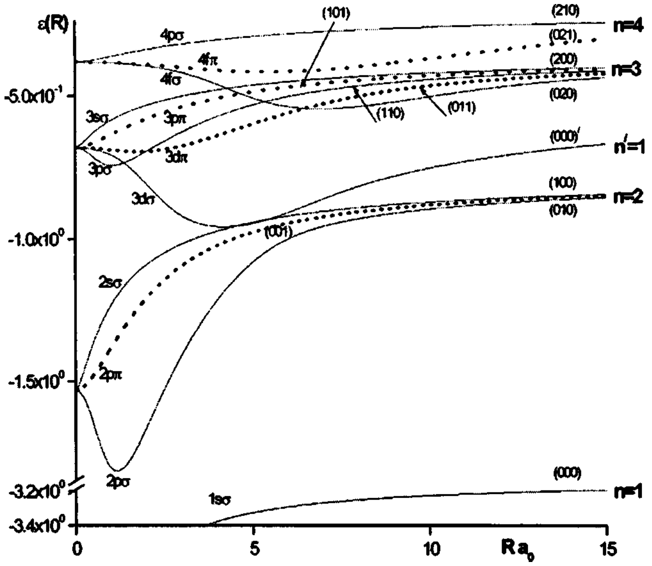

FIG. 3. Molecular orbital correlation diagram for the quasimolecule $Z_{1e}Z_2$ with $Z_1=2.5$ and $Z_2=1$. The notations are similar to the ones on Fig. 1.

Let us emphasize some conclusions useful for experiments. The entire spectra produced by heteronuclear quasimolecules are richer than those in the homonuclear case, essentially due to the exhibition of the former forbidden g-g and u-u transitions. The most prominent features of the spectra are line cores produced by transitions emitted by isolated ions. The wings produced by quasimolecular transitions can be estimated by the well-known quasistatic approximation. Within this assumption, the spectral profile in emission may be written as

$$I_{if}(\Delta\omega) \sim R_c^2 \frac{A_{if}(R_c)}{\left|\frac{d\Delta U_{if}}{dR}\right|_{R_c}} e^{-U_i(R_c)/T}. \tag{20}$$

Here $\Delta\omega=\omega-\omega_0$ represents the shift from the single-ion transition frequency, and, $\Delta U_{if}=U_i-U_f$ is taken for the Condon point R_c, i.e., $\Delta\omega=\Delta U_{if}(R_c)$.

Therefore, the existence of zeros in the dipole matrix elements leads to zeros in the wings of the spectral lines. It is obvious that this last conclusion is based on the quasistatic approximation. In fact the zeros in the spectral profiles will be replaced by minima of intensity, i.e., dips in the spectra, even in the semiclassical approach [22].

We must stress that the description of the line cores of allowed transitions is beyond the quasistatic approximation, but in the case of forbidden quasimolecular transitions the whole spectral profiles can be estimated by Eq. (20).

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APPENDIX

When R tends to infinity, each of the considered two-Coulomb-center wave functions transforms itself into the relevant parabolic eZ monocenter wave function. These parabolic functions are determined as follows [14]:

$$\varphi_{n_1n_2m} = \frac{2^{1/2}Z^{3/2}}{n^2} f_{n_1m}\left(\frac{Z\mu}{n}\right) f_{n_2m}\left(\frac{Z\nu}{n}\right) e^{im\varphi}/\sqrt{2\pi}, \quad \text{(A1)}$$

$$f_{nm}(\rho) = \frac{1}{m!}\sqrt{\frac{(n+m)!}{n!}} e^{-\rho/2}\rho^{m/2} F(-n,m+1,\rho). \quad \text{(A2)}$$

Here $n_{1,2}, m$ are parabolic quantum numbers with $n_1+n_2+m+1=n$, and $F(-n,m+1,\rho)$ is the confluent hypergeometric function.

The transition-matrix element for parallel transitions between the states with parabolic numbers (n_1n_20) and $(n_1'n_2'0)$ is given by

$$\begin{aligned}\langle n_1n_20|d_z|n_1'n_2'0\rangle = &= \frac{1}{4n^2n'^2}\int_0^\infty\int_0^\infty (\xi^2-\eta^2) f_{n_10}\left(\frac{\xi}{n_1}\right) \\ &\times f_{n_1'0}\left(\frac{\xi}{n_1'}\right) f_{n_20}\left(\frac{\eta}{n_2}\right) f_{n_2'0}\left(\frac{\eta}{n_2'}\right) d\xi\, d\eta. \end{aligned} \quad \text{(A3)}$$

Therefore

$$\langle n_1n_20|d_z|n_1'n_2'0\rangle = -\langle n_2n_10|d_z|n_2'n_1'0\rangle. \quad \text{(A4)}$$

For transitions involving the ground state the explicit expression of the matrix element is given by

$$\begin{aligned}\langle n_1n_20|d_z|000\rangle = \frac{8n^2}{(n+1)^4Z}\Bigg[& F\left(-n_1,1,1,\frac{2}{n+1}\right) \\ &\times F\left(-n_2,3,1,\frac{2}{n+1}\right) \\ &- F\left(-n_2,1,1,\frac{2}{n+1}\right) \\ &\times F\left(-n_1,3,1,\frac{2}{n+1}\right)\Bigg]. \end{aligned} \quad \text{(A5)}$$

In a similar way we get for the perpendicular transitions

$$\langle n_1n_21|d_x|n_1'n_2'0\rangle = \langle n_2n_11|d_x|n_2'n_1'0\rangle \quad \text{(A6)}$$

and for transitions involving the ground state

$$\begin{aligned}\langle n_1n_21|d_x|000\rangle = &\frac{16n^2}{(n+1)^5Z}\sqrt{\frac{(n_1+1)!(n_2+1)!}{n_1!n_2!}} \\ &\times\left[F\left(-n_1,2,2,\frac{2}{n+1}\right)F\left(-n_2,3,2,\frac{2}{n+1}\right)\right. \\ &\left.+F\left(-n_2,2,2,\frac{2}{n+1}\right)F\left(-n_1,3,2,\frac{2}{n+1}\right)\right]. \end{aligned} \quad \text{(A7)}$$

Here $F(-n,a,b,2/(n+1))$ is the hypergeometric function.

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