A pseudopotential hole-particle treatment of neutral rare gas excimer systems. I. Formalism

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A pseudopotential hole-particle formalism is developed for the treatment of rare-gas excimers and excited rare-gas clusters. The formalism relies on the definition of a model Hamiltonian on the basis of single hole-particle excitations (from the neutral closed shell ground state) involving localized np hole orbitals and any orthogonal molecular orbital (MO) basis set for the excited particle. Hole contributions in the Hamiltonian matrix elements are taken into account via distance- and orientation-dependent transfer integrals (hole delocalization) and repulsion integrals like in diatomic in molecules treatments of rare gas ions, while the contribution of the excited particle is included through an explicit quantal treatment via one-electron e-Rg and averaged e-Rg$^+$ pseudopotentials. Core-polarization pseudopotentials are also added to account for core-polarization and core-Rydberg correlation effects. Some approximated core-Rydberg two-electron integrals needed for adequate space and spin multiplicity of the excited states are also included. The possible applications and extensions of this formalism are discussed. © *1996 American Institute of Physics.* [S0021-9606(96)01827-2]

I. INTRODUCTION

The spectroscopy of rare gas systems has been the object of a continuous work since the pioneering experimental study of Tanaka *et al.*[1] and the theoretical predictions of Mulliken on the Xe$_2^*$ excimer.[2] One early reason for this interest was the potential application of excimers in laser sources to produce emission in the VUV spectrum. As sketched by Mulliken,[2] the excited electronic states of rare gas dimers can be understood as resulting from the interaction of an ionic compact core (Rg$_2^+$) with a rather diffuse Rydberg electron. Without spin–orbit coupling, the dimer positive ion has four electronic states, namely $^2\Sigma_u^+$, $^2\Pi_g$, $^2\Pi_u$, and $^2\Sigma_g^+$. From a qualitative point of view, the adiabatic excited states of Rg$_2^*$ can thus be considered as resulting from the interaction of diabatic Rydberg series converging toward those four positive ion states. A renewed interest in the electronic structure of excited rare gas systems was recently brought in the field of cluster physics as prototypes of excitonic systems bridging the dimer and the well-known bulk properties. The region of a few ten rare gas atoms is particularly interesting from this point of view.

From a theoretical aspect, the difficulty lies in the number of electrons per atom in those clusters. Even using usual valence pseudopotentials or effective core potentials, each rare gas atom is an eight-electron system (seven when ionized) and the problem quickly reaches a prohibitive size. Beyond dimers, mainly ionic trimers for the moment have received to our knowledge full *ab initio* treatment.[3–13] Even in the case $n=3$ only, ambiguities have arisen in *ab initio* studies[12] to decide whether the geometrical structure of Ar$_3^+$, for instance, is linear symmetric ($D_{\infty h}$) or linear asymmetric ($C_{\infty V}$) and it appears that very accurate calculations involving extensive CI are necessary. Very few *ab initio* CI investigations were attempted on systems larger than trimers.[13,14]

Thus, theoreticians had to develop models to deal with large systems. One of the most successful method for singly charged species is the diatomic in molecules (DIM) method early used by Wadt on trimers,[15] and more recently applied[3–27] by several authors for larger clusters like Ne$_N^+$,[26] Ar$_N^+$,[26] Xe$_N^+$,[23] eventually incorporating spin–orbit coupling. The success of the DIM method in such cases relies on the fact that the valence states of an ionic cluster can be spanned on a basis of holes (with respect to the neutral closed shell van der Waals ground state) in the valence atomic np orbitals localized on the different atoms of the cluster. One usually uses the useful but noncompulsory approximation that the np atomic orbitals form an orthogonal set. Thus, the ground state electronic and geometrical structure of the ionic rare gas clusters could be investigated, demonstrating that the final delocalization of the hole in those clusters only reaches small linear subunits, such as dimers, linear trimers or tetramers around which the other almost neutral atoms can arrange within crowns, which are completed for $N=13$ and $N=19$. The valence excited states of the charged clusters are also correctly accounted for in the DIM model.[24–28] Moreover, due to its weak complexity (the DIM matrix has a $3N \times 3N$ size in the nonrelativistic case and $6N \times 6N$ size if spin–orbit coupling is included), even dynamical simulations such as Monte Carlo or molecular dynamics for simulating the absorption spectra could be achieved.[29,30] The capability of DIM calculations to reproduce *ab initio* results was confirmed recently through systematic comparisons involving trimer and tetramer potential energy surfaces (PES) by Naumkin *et al.*,[12] concluding to a satisfactory reliability of the method, except for the lightest system He$_3^+$.

A few similar DIM studies were attempted in the case of rare gas neutral excited clusters.[31,32] When applying the DIM

method to neutral rare gas excitations, the final wave function is generally expressed as a combination of localized hole-particle states (from the ground state reference), and the main physics involved concerns the hopping of this atom-localized hole-particle excitation within the cluster. This may be a first drawback, since if the localization of the hole is physically sounded, the Rydberg diffuse electron is not actually localizable on a single center. The localization of the electron on the very same site as the hole brings a strong constraint in the final wave function, since the delocalization of the Rydberg electron is *a priori* coupled to that of the hole. Another difficulty in Rydberg situation is the problem of transferability. Indeed, it is not at all quite sure that dimer-based matrix elements are transferable to larger clusters, since the excited electron orbital is expected to be rather diffuse and delocalized. Moreover, unlike in the ionic dimer, where the four molecular valence states keep a constant hole nature, the potential curves of the neutral excited dimer, even those correlated with the lowest atomic excited configuration $np^5(n+1)s$, undergo configuration mixing in particular with the $np^5(n+1)p$ configuration. They can by no means be considered as diabatic with respect to the asymptotic dissociation. Thus, if one constructs a DIM model involving a basis built from a single type of excitations ($3p^54s$ for instance in the case of argon), one faces the risk at short internuclear distance of a mismatch between the content of the input dimer data necessary for the DIM code and the nature of the implicit wave-function basis in the DIM treatment. However, extension to DIM models involving the $np^5(n+1)p$ excitations is more cumbersome and has not yet been achieved. Furthermore, the situation becomes more and more intricated when one considers higher excited states since more and more ''intruder'' states undergo avoided crossings and make proper assignment almost unfeasible and also because dimer data in the relevant range become either very difficult to manipulate or even not available.

An alternative approach to excited states in excimer or exciplex systems was based on model potential calculations[33–41] following techniques extensively used in the study of alkali dimers and alkali rare gas dimers. This technique has also received a new motivation with the possibility of providing for some classes of systems very accurate results in relationship with experiments observing the interaction between extremely cold atoms. In such schemes, the excited rare gas dimers are considered as one-electron systems and involve two model potentials. The first one acts between the excited electron and an Rg$^+$ ion. The second one represents the electron-neutral e-Rg atom interaction. Some systems such as HeNe* (Ref. 40) or Ne$_2^*$ (Ref. 41) were investigated within this framework. The determination of those model potentials was achieved semi-empirically. They could thus produce very accurate results in the long range region, but up to now, the study of the short range region has not be achieved. Taking the example of homogeneous dimers, for instance, calculations have been restricted to consider disymmetrized situations such as Rg*Rg where the electron interacts with a hole created on the first atom and they still rely on the asymptotic limit in which the neu-

tral atom is considered as a perturbator. This is more and more questionable when the distance is reduced. Obviously, one should consider the resonance between the two degenerate and equivalent situations Rg*Rg and RgRg* as well known in the valence-bond theory and include the core interactions which become dominant at short distance.

In the present work (paper I), we wish to extend the applicability range of pseudopotential methods in this direction. We present a hole-particle model Hamiltonian for treating neutral rare gas excimers. It considers hole-particle single excitations. The holes, as in the DIM model for ions, are supposed to be localizable on the atomic sites, but no such assumption is made with respect to the localization of the Rydberg electron. The model does not imply *a priori* hypothesis about the correlation between the respective localization or delocalization of the hole or the electron. The Hamiltonian is twofold, implying core contributions which will receive a treatment analogous to the DIM model, and the excited electron contribution which is treated explicitly by means of one-electron pseudopotentials. Those one-electron pseudopotentials are defined in a framework where all electrons usually defined as valence electrons are considered in the core, the Rydberg electron excepted. Moreover, in addition, the most important two-electron contributions, responsible for atomic intramultiplet splitting, intra- and interconfigurational molecular couplings, are also considered within simplified schemes. Core-polarization pseudopotentials (CPP) are incorporated, accounting for core-polarization and core-Rydberg correlation. The model also involves spin–orbit coupling, in order to be able to cope with the heavier rare gas atoms. Section II presents a partition of the Hamiltonian which allows for a decoupling of the interactions in rare gas clusters (core–core interactions, core-Rydberg interactions, hole transfer, excitation transfer) and on which the model is based. Section III explicits the model and the incorporation of the one-electron averaged pseudopotentials and core-polarization pseudopotentials. Section IV details the numerical implementation in the case of argon for the treatment of the Rydberg states of the Ar$_2^*$ excimer developed in a second article (paper II) and in further investigations of argon clusters.

II. PARTITION OF THE HAMILTONIAN

The total Hamiltonian for an excited homogenous N-atom system is expressed as

$$H_T = H_{\text{el}} + H_{\text{SO}}.$$

We first present the derivation of H_{el}. We shall label $\chi_{A\mu\zeta}$ the valence np spin–orbitals ($n=3$ for Ar), where A refers to a particular atomic site ($1 \leq A \leq N$), μ refers to the spatial orientation ($\mu=x,y,z$) and ζ characterizes the spin projection. Those atomic spin–orbitals will be assumed to be orthonormal:

$$\langle \chi_{A\mu\zeta} | \chi_{B\nu\sigma} \rangle = \delta_{AB} \delta_{\mu\nu} \delta_{\zeta\sigma}.$$

Given a set of $2M$ orthonormal Rydberg molecular spinorbitals $\{\phi_{i\alpha}\}$ where α denotes the spin projection and i labels the orbital ($1 \leq i \leq M$), one may define a hole-particle basis:

$$|\Phi_{A\mu\zeta}^{i\alpha}\rangle = a_{i\alpha}^{+}a_{A\mu\zeta}|\Phi_0\rangle,$$

which defines a single excitation obtained from the neutral van der Waals ground state $|\Phi_0\rangle$ through the creation of a localized hole in spin–orbital $\chi_{A\mu\zeta}$ and the promotion of an electron in one of the Rydberg spin–orbitals $\phi_{i\alpha}$. The Hamiltonian is expressed in this basis set:

$$H_{A\mu\zeta,B\nu\sigma}^{i\alpha,j\beta} = \langle\Phi_{A\mu\zeta}^{i\alpha}|H_{\text{el}}|\Phi_{B\nu\sigma}^{j\beta}\rangle.$$

The diagonal elements can be decomposed as

$$H_{A\mu\zeta,A\mu\zeta}^{i\alpha,i\alpha} = \langle\Phi_{A\mu\zeta}^{i\alpha}|H_{\text{el}}|\Phi_{A\mu\zeta}^{i\alpha}\rangle$$

$$= E_A^+ + \sum_{B\neq A} E_B + \sum_{B\neq A} V_{\mu\zeta}^+(AB)$$

$$+ \sum_{B\neq A}\sum_{C\neq A,C>B} V(BC) + h_{A\mu\zeta}^{i\alpha,i\alpha}.$$

The first term corresponds to the energy of the ionized atom:

$$E_A^+ = \sum_{\nu\sigma\neq\mu\zeta} \langle\chi_{A\nu\sigma}|-\frac{\Delta}{2}-\frac{Z_A}{r_A}|\chi_{A\nu\sigma}\rangle$$

$$+ \sum_{\nu\sigma\neq\mu\zeta}\sum_{\lambda\xi\neq\mu\zeta} (\langle\chi_{A\nu\sigma}\chi_{A\lambda\xi}|\chi_{A\nu\sigma}\chi_{A\lambda\xi}\rangle$$

$$- \langle\chi_{A\nu\sigma}\chi_{A\lambda\xi}|\chi_{A\lambda\xi}\chi_{A\nu\sigma}\rangle).$$

The second term is the sum of the energies of the neutral ground state atoms

$$E_B = \sum_{\nu\sigma} \langle\chi_{B\nu\sigma}|-\frac{\Delta}{2}-\frac{Z_B}{r_B}|\chi_{B\nu\sigma}\rangle$$

$$+ \sum_{\nu\sigma}\sum_{\lambda\xi} (\langle\chi_{B\nu\sigma}\chi_{B\lambda\xi}|\chi_{B\nu\sigma}\chi_{B\lambda\xi}\rangle$$

$$- \langle\chi_{B\nu\sigma}\chi_{B\lambda\xi}|\chi_{B\lambda\xi}\xi_{B\nu\sigma}\rangle).$$

The third term stands for the interactions between the ionized atom and the neutral ones

$$V_{\mu\zeta}^+(AB) = \sum_{\nu\sigma\neq\mu\zeta} \langle\chi_{A\nu\sigma}|-\frac{Z_B}{r_B}|\chi_{A\nu\sigma}\rangle$$

$$+ \sum_{\nu\sigma} \langle\chi_{B\nu\sigma}|-\frac{Z_A}{r_A}|\chi_{B\nu\sigma}\rangle$$

$$+ \sum_{\nu\sigma\neq\mu\zeta}\sum_{\lambda\xi} (\langle\chi_{A\nu\sigma}\chi_{B\lambda\xi}|\chi_{A\nu\sigma}\chi_{B\lambda\xi}\rangle$$

$$- \langle\chi_{A\nu\sigma}\chi_{B\lambda\xi}|\chi_{B\lambda\xi}\chi_{A\nu\sigma}\rangle).$$

The fourth term represents the sum of the interactions between the neutral atoms:

$$V(BC) = \sum_{\nu\sigma} \langle\chi_{B\nu\sigma}|-\frac{Z_B}{r_B}|\chi_{C\nu\sigma}\rangle$$

$$+ \sum_{\nu\sigma}\sum_{\lambda\xi} (\langle\chi_{B\nu\sigma}\chi_{C\lambda\xi}|\chi_{B\nu\sigma}\chi_{C\lambda\xi}\rangle$$

$$- \langle\chi_{B\nu\sigma}\chi_{C\lambda\xi}|\chi_{C\lambda\xi}\chi_{B\nu\sigma}\rangle).$$

The last term corresponds to the energy of the excited electron and its interaction with the rest of the system (hereafter called the core)

$$h_{A\mu\zeta}^{i\alpha,i\alpha} = \langle\phi_{i\alpha}|-\frac{\Delta}{2}|\phi_{i\alpha}\rangle + \langle\phi_{i\alpha}|-\frac{Z_A}{r_A}|\phi_{i\alpha}\rangle + \sum_A\sum_{\lambda\xi\neq\mu\zeta} (\langle\phi_{i\alpha}\chi_{A\lambda\xi}|\phi_{i\alpha}\chi_{A\lambda\xi}\rangle - \langle\phi_{i\alpha}\chi_{A\lambda\xi}|\chi_{A\lambda\xi}\phi_{i\alpha}\rangle)$$

$$+ \sum_B \left\{ \langle\phi_{i\alpha}|-\frac{Z_B}{r_B}|\phi_{i\alpha}\rangle + \sum_{\lambda\xi} (\langle\phi_{i\alpha}\chi_{B\lambda\xi}|\phi_{i\alpha}\chi_{B\lambda\xi}\rangle - \langle\phi_{i\alpha}\chi_{B\lambda\xi}|\chi_{B\lambda\xi}\phi_{i\alpha}\rangle) \right\}.$$

The nonvanishing off-diagonal elements which involve only one-hole differences contribute to the hole delocalization (hopping integrals). They can be written as

$$H_{A\mu\zeta,B\nu\zeta}^{i\alpha,i\alpha} = F_{\mu\nu}^+(AB) + \sum_{C\neq A,B} F_{\mu\nu}^+(AB,C) + \langle\chi_{A\mu\zeta}\phi_{i\alpha}|\chi_{B\nu\zeta}\phi_{i\alpha}\rangle - \langle\chi_{A\mu\zeta}\phi_{i\alpha}|\phi_{i\alpha}\chi_{B\nu\zeta}\rangle,$$

where the first term is the two-body core contribution

$$F_{\mu\nu}^+(AB) = \langle\chi_{A\mu\zeta}|-\frac{\Delta}{2}-\frac{Z_A}{r_A}-\frac{Z_B}{r_B}|\chi_{B\nu\zeta}\rangle + \sum_{\lambda\xi\neq\mu\zeta} (\langle\chi_{A\mu\zeta}\chi_{A\lambda\xi}|\chi_{B\nu\zeta}\chi_{A\lambda\xi}\rangle - \langle\chi_{A\mu\xi}\chi_{A\lambda\xi}|\chi_{A\lambda\xi}\chi_{B\nu\zeta}\rangle)$$

$$+ \sum_{\lambda\xi\neq\nu\zeta} (\langle\chi_{A\mu\zeta}\chi_{B\lambda\chi}|\chi_{B\nu\zeta}\chi_{B\lambda\xi}\rangle - \langle\chi_{A\mu\zeta}\chi_{B\lambda\xi}|\chi_{B\lambda\xi}\chi_{B\nu\zeta}\rangle).$$

The second term accounts for three-body core contributions

$$F_{\mu\nu}^+(AB,C) = \langle\chi_{A\mu\zeta}|-\frac{Z_C}{r_C}|\chi_{B\nu\zeta}\rangle + \sum_{\lambda\xi} (\langle\chi_{A\mu\zeta}\chi_{C\lambda\xi}|\chi_{B\nu\zeta}\chi_{C\lambda\xi}\rangle - \langle\chi_{A\mu\zeta}\chi_{C\lambda\xi}|\chi_{C\lambda\xi}\chi_{B\nu\zeta}\rangle).$$

The last terms provide the Rydberg-core contributions to the matrix elements.

One also has matrix elements involving one-particle differences:

$$h_{A\mu\zeta}^{i\alpha,j\alpha}=\langle\phi_{i\alpha}|-\frac{\Delta}{2}|\phi_{j\alpha}\rangle+\langle\phi_{i\alpha}|-\frac{Z_A}{r_A}|\phi_{j\alpha}\rangle+\sum_A\sum_{\xi\neq\mu\zeta}(\langle\phi_{i\alpha}\chi_{A\lambda\xi}|\phi_{j\alpha}\chi_{A\lambda\xi}\rangle-\langle\phi_{i\alpha}\chi_{A\lambda\xi}|\chi_{A\lambda\xi}\phi_{j\alpha}\rangle)$$

$$+\sum_B\left\{\langle\phi_{i\alpha}|-\frac{Z_B}{r_B}|\phi_{j\alpha}\rangle+\sum_{\lambda\xi}(\langle\phi_{i\alpha}\chi_{B\lambda\xi}|\phi_{j\alpha}\chi_{B\lambda\xi}\rangle-\langle\phi_{i\alpha}\chi_{B\lambda\xi}|\chi_{B\lambda\xi}\phi_{j\alpha}\rangle)\right\}.$$

Finally, remain the nonvanishing off-diagonal matrix elements involving two differences respectively:

$$\langle\phi_{i\alpha}\chi_{A\mu\xi}|\phi_{j\beta}\chi_{B\nu\lambda}\rangle\delta_{\alpha\beta}\delta_{\xi\lambda}-\langle\phi_{i\alpha}\chi_{A\mu\xi}|\chi_{B\nu\lambda}\phi_{j\beta}\rangle\delta_{\alpha\lambda}\delta_{\xi\beta}.$$

Until this step, the expressions relying on a minimal basis set description of the hole orbitals remain basically exact, and all matrix elements could be evaluated like in *ab initio* calculations. We now choose to treat separately in each matrix element the core part, corresponding to Rg_N^+ and the Rydberg part corresponding to the Rydberg electron.

III. HOLE-PARTICLE PSEUDOPOTENTIAL FORMALISM

A. Diatomic in molecules treatment of the core

The np valence atomic orbitals are relatively compact and do not overlap strongly in the relevant range of distance. We thus use for the core a diatomic in molecules (DIM) approximation which essentially consists in neglecting the three-body terms in the above equations, exactly as in previous works dealing with Rg_N^+ rare gas clusters and determining the two-body terms from their isolated dimer equivalents. Following the formulation given by Amarouche *et al.*,[23] for each pair AB the $V_\mu^+(AB)$ and $F_{\mu\nu}^+(AB)$ terms can be obtained from the $V_\Sigma^+(AB)$ and $V_\Pi^+(AB)$ through a proper rotation [with unitary matrix $U(AB)$] mapping the fixed cartesian orthogonal frame into an orthogonal frame associated with the AB direction.

$$V_\mu^+(AB)=\sum_\lambda U_{\lambda\mu}^\dagger V_\lambda^+(AB)\quad(\lambda=\Sigma,\Pi_x,\Pi_y).$$

In the same way, one can determine the hopping integrals $F_{\mu\nu}^+(AB)$ for different orientations of the μ and ν holes from the $F_{\Sigma\Sigma}^+(AB)$ and $F_{\Pi\Pi}^+(AB)$ on the dimer

$$F_{\mu\nu}^+(AB)=\sum_\lambda U_{\lambda\mu}^\dagger U_{\lambda\nu}F_{\lambda\lambda}^+(AB)\quad(\lambda=\Sigma,\Pi_x,\Pi_y).$$

The $V_\Sigma^+(R)$, $V_\Pi^+(R)$, $F_{\Sigma\Sigma}^+(R)$, and $F_{\Pi\Pi}^+(R)$ are then simple functions of R that can be taken from experiment or *ab initio* calculations.

The neutral–neutral interactions $V(AB)$ are isotropic and can be obtained in the case of rare gas atom pairs using empirical multiproperty fits which are at present time still more accurate for heavy van der Waals systems than most *ab initio* determinations, at least in the ground state bound region where empirical potentials are fitted on spectroscopic data.

B. Pseudopotential treatment of the Rydberg electron

Both diagonal and off-diagonal particle contributions in the above equations can be expressed with the help of an open-shell Fock operator:

$$F_{A\mu\zeta}^*=-\frac{\Delta}{2}-\frac{Z_A}{r_A}+\sum_{\lambda\xi\neq\mu\zeta}(J_{A\lambda\xi}-K_{A\lambda\xi})$$

$$+\sum_{B\neq A}\left\{-\frac{Z_B}{r_B}+\sum_{\lambda\xi}(J_{B\lambda\xi}-K_{B\lambda\xi})\right\}.$$

This operator characterizes the interaction of a Rydberg electron with a space and spin-polarized hole in spin–orbital $\chi_{A\mu\zeta}$. It is convenient to define an isotropic space and spin-averaged pseudopotential where the Coulomb and exchange operators are averaged on different space and spin orientations:

$$F_A^*=\frac{1}{6}\sum_{\mu\zeta}F_{A\mu\zeta}^*.$$

The matrix elements of the total Hamiltonian can be easily derived from F_A^* with the help of a few two-electron integrals restoring the hole anisotropy:

$$H_{A\mu\zeta,A\mu\zeta}^{i\alpha,j\alpha}=\langle\phi_{i\alpha}|F_A^*|\phi_{j\alpha}\rangle+\langle\phi_{i\alpha}|F_{A\mu\zeta}^*-F_A^*|\phi_{j\alpha}\rangle.$$

Now the all-electron averaged Fock operator is substituted by a pseudopotential for the Rydberg electron, replacing the frozen electrons of ionized core A^+ and of the neutral atoms B:

$$f_A^*=-\frac{\Delta}{2}-\frac{1}{r_A}+W_A^++\sum_{B\neq A}W_B.$$

$-1/r_A+W_A^+$ represents the interaction of the Rydberg electron with a frozen isotropic ion A^+ and W_B represents its interaction with the frozen neutral atoms. It achieves the repulsion to the core orbitals.

The determination of the one-electron pseudopotential within a nodeless pseudo-orbital scheme is detailed in Sec. IV. There are two effects beyond this frozen isotropic hole that deserve to be taken into account. The first one is the polarization of the electrons of the ionic core and of the neutral atoms as well as their correlation with the explicitly treated Rydberg electron. This is achieved via a core-polarization operator[42] according to the l-dependent method proposed by Foucrault *et al.*[43] In the present system, a core-polarization operator $f_{A,\mathrm{pol}}$ depending on the localization of the hole is added to f_A^*:

$$f_{A,\text{pol}} = -\tfrac{1}{2}\alpha_A^+ \mathbf{E}_A^2 - \sum_{B \neq A} \tfrac{1}{2}\alpha_B \mathbf{E}_B^2,$$

where

$$\mathbf{E}_A = -\sum_{l,m} \frac{\mathbf{r}_A}{r_A^3} \Theta(r_A - \rho_{c,l}^+)|Y_{lm}^{(A)}\rangle\langle Y_{lm}^{(A)}|$$

and

$$\mathbf{E}_B = \frac{\mathbf{R}_{AB}}{R_{AB}^3} - \sum_{l,m} \frac{\mathbf{r}_B}{r_B^3} \Theta(r_B - \rho_{c,l})|Y_{lm}^{(B)}\rangle\langle Y_{lm}^{(B)}|$$

are the electric field operator on the ionic atom A and on the neutral atoms B respectively. α^+ and α are the respective dipole polarizabilities of the ionized Rg^+ and neutral Rg atoms. $\rho_{c,l}^+$ and $\rho_{c,l}$ which appear in the Θ step functions are the l-dependent cut-off radii for Rg^+ and Rg respectively, which prevent electric field integrals to diverge in the vicinity of the nuclei.

The second extension is the introduction of some two-electron integrals to go beyond the isotropic hole scheme. Approximations for those integrals are explicited in the next subsection.

C. Approximations for two-electron integrals

One needs an evaluation of the two electron integrals in order to: (i) consider the exchange contributions and achieve spin multiplet splitting (ii) consider spatial hole particle anisotropy and achieve spatial multiplet splitting. Those are the conditions for an adequate symmetry description of the molecular states in the whole distance range.

One solution is of course to compute those integrals *ab initio*, considering frozen explicit atomic np hole orbitals and the present one-electron molecular orbitals (however not orthogonal to the np holes because of the nodeless pseudo-orbital framework). One should also incorporate two-center contributions. Those are necessary for an accurate treatment of the long range forces and play a role in exciton dynamics of rare gas clusters. However, this of course burdens the calculation in non trivial Rg_N^* clusters.

Consistently with the current formalism, we propose to neglect all integrals involving hole overlaps on different centers (INDO type approximation for the holes). One is then left with direct or exchange integrals such as

$$\langle \phi_i \chi_{A\mu} | \phi_j \chi_{A\nu} \rangle \quad \text{or} \quad \langle \phi_i \chi_{A\mu} | \chi_{A\nu} \phi_j \rangle,$$

where the hole is localized on atom A and the Rydberg orbital ϕ_i is in general delocalized. We develop here two types of approximation, avoiding the explicit calculation of the molecular integrals.

The first one (method A) consists in an one-center expansion of the Rydberg molecular orbitals ϕ_i and ϕ_j on the atomic Rydberg orbitals basis set $\{\phi_{Ap}\}$ of atom A for computing integrals involving holes on A.

$$\langle \phi_i \chi_{A\mu} | \phi_j \chi_{A\nu} \rangle = \sum_p \sum_q c_{pi}^* c_{qj} \langle \phi_{Ap} \chi_{A\mu} | \phi_{Aq} \chi_{A\nu} \rangle$$

or

$$\langle \phi_i \chi_{A\mu} | \chi_{A\nu} \phi_j \rangle = \sum_p \sum_q c_{pi}^* c_{qj} \langle \phi_{Ap} \chi_{A\mu} | \chi_{A\nu} \phi_{Aq} \rangle$$

with $c_{pi} = \langle \phi_{Ap} | \phi_i \rangle$ and the restriction that ϕ_{Ap} and ϕ_{Aq} belong to the same atomic configuration (no interconfigurational coupling on the atom).

The second method (method B) consists in evaluating the integrals by means of operatorial techniques. For each direct or exchange above defined integral involving holes $\chi_{A\nu}$ and $\chi_{A\mu}$, we define a set of atomic operators in semi-local form:

$$\Gamma_{\mu\nu}^{(A)} = \sum_l \sum_{m,k} \Gamma_{\mu\nu,km}^{(l)}(r) P_{km}^{(l)}.$$

The $P_{km}^{(l)}$ are projectors on spherical harmonics of the particle on center A:

$$P_{km}^{(l)} = |Y_{lm}^{(A)}\rangle\langle Y_{lk}^{(A)}|.$$

The radial parts $\Gamma_{\mu\nu,km}^{(l)}(r)$ are expanded as combinations of Gaussian functions.

D. Spin–orbit coupling

The spin–orbit coupling magnitude for the hole orbitals is much larger than for the Rydberg orbitals. In the case of atomic Argon, ζ_{3p} is 954 cm^{-1}, whereas ζ_{4p}, the largest Rydberg parameter is only 26 cm^{-1} (as obtained through a fit to the experimental atomic data). Thus, we neglected all contributions from Rydberg orbitals (particles) and only considered the spin–orbit contributions of the holes according to the atoms in molecules (AIM) scheme first developed by Cohen and Schneider[44] and already used in DIM treatments of Rg_N^+ clusters including fine structure,[30–36] incorporated here in a diabatic-like picture for the holes.

$$(H_{\text{SO}})_{A\mu\zeta,B\nu\sigma}^{i\alpha,j\beta} = \langle \chi_{\mu\zeta} | h_{\text{SO}} | \chi_{\nu\sigma} \rangle \delta_{ij} \delta_{AB} \delta_{\alpha\beta}.$$

The hole spin–orbit coupling operator h_{SO} is an effective intra-atomic single-particle operator:

$$h_{\text{SO}} = \zeta_{np} \hat{l} \cdot \hat{s}.$$

The eigenvalues and eigenstates are finally obtained by diagonalizing a $12NM \times 12NM$ complex matrix.

$$(H_{\text{el}} + H_{\text{SO}})\Psi_m = E_m \Psi_m,$$

$$\Psi_m = \sum_{A\mu\zeta,i\alpha} C_{A\mu\zeta}^{i\alpha m} \Phi_{A\mu\zeta}^{i\alpha}.$$

IV. NUMERICAL IMPLEMENTATION FOR ARGON

We provide in this section the technical and numerical details of the implementation of the method in the case of argon.

A. e-Rg^+ pseudopotential

The electron $-Ar^+$ pseudopotential was extracted from all-electron averaged relativistic[45] Hartree–Fock calculations for the lowest states with an excited atomic orbital charac-

TABLE I. One-electron pseudopotential parameter $W_1(r) = \exp(-\alpha r^2)\Sigma_i c_i r^{n_i}$ and core polarization pseudopotential cut-off radii $\rho_{c,1}$.

l	n_1	c_1	n_2	c_2	α	$\rho_{c,1}^+$
		e-Ar$^+$ pseudopotential data				
0	0	1.049 1485	1	3.408 3423	0.621 471 12	2.5195
1	0	−0.229 081 05	1	1.552 9626	0.374 433 26	2.853
2	−1	−5.790 7947			0.687 681 07	1.86

l	n_1	c_1	α	$\rho_{c,1}$
		e-Ar pseudopotential data		
0	0	52.799 655	1.353 56	3.1704
1	0	1.103 546	0.211 596	2.5914
2	−1	−1.103 546	0.207 388	1.4

terized by $l=1$, 2 and 3 symmetries, namely configurations $3p^5 4s$, $3p^5 4p$, and $3p^5 3d$. The actual orbitals and one-electron energies were taken as the virtual levels of the Rg$^+$ ion calculated with the averaged all-electron operator F_A^+. Nodeless pseudo-orbitals with smooth inner part and shape-consistent, l-dependent pseudopotentials were obtained using the Durand and Barthelat[46] formalism. There is no technical difference with classical pseudopotential extraction for valence electrons, except the fact that the extension of the Rydberg atomic orbitals is much larger than that of the usual valence orbitals and requires of course an extensive diffuse basis set. The pseudopotential parameters are listed in Table I.

Afterwards, the l-dependent cut-off radii $\rho_{c,l}^+$ in the polarization operator were determined in order to reproduce the ''experimental'' averaged configurational energies, extracted from the experimental data tables.[47] The dipole polarizability for Ar$^+$ was taken as 7.895 a_0^3. The Gaussian basis set used for the atomic Rydberg states is an uncontracted $10s/10p/11d$ listed in Table II. Indicated contractions will be carried on in the molecular calculation of paper II. We have checked the transferability of the pseudopotentials to higher excited states and it is seen in Table III that this transferability is achieved within a few ten cm^{-1}.

B. e-Ar pseudopotential

Since the negative ion does not exist, we have extracted the electron-argon pseudopotential as well as the associated core-polarization pseudopotential by reproducing elastic e-Ar scattering properties, namely phase shifts which are l-dependent data. We chose, as recommended by De Chebannier and Masnou-Seuuws[39] who worked in the model potential framework a set of data in a rather wide collision energy range between 0.005 and 10 eV. The process is quite similar to the work of Czuchaj et al.[48] for e-Rg pseudopotentials, with some technical differences. First, the phase-shift data used in the determination of the pseudopotentials involve a wider energy range. Also, the core-polarization pseudopotentials are l-dependent and the cut-off radii have different analytic shape.[43] The neutral argon polarizability was taken at 11.08 a_0^3. The e-Ar pseudopotential was found to provide accurate results on the NaAr system which will be discussed elsewhere. The pseudopotentials parameters for e-Ar and the cut-off radii are displayed in Table I.

C. Two-electron integrals

The atomic two-electron integrals values were calculated ab initio for $3p^5 ns$ and $3p^5 np$ configurations (n=4–8). In-

TABLE II. Gaussian basis set on Ar.

s type		p type		d type	
Exponent	Contraction coefficients	Exponent	Contraction coefficients	Exponent	Contraction coefficients
7.420 225	0.001 04	7.420 225	0.000 16	4.826	0.005 59
0.786	−0.041 03	0.786	−0.004 41	2.041	0.015 14
0.551	0.262 61	0.551	0.028 42	1.0815	0.022 46
0.36	−0.378 79	0.36	−0.033 56	0.664	0.022 19
0.155	−0.150 91	0.155	−0.073 91	0.333	0.033 44
0.08		0.07	0.087 37	0.150	0.040 41
0.04		0.035		0.080	0.066 51
0.015		0.016		0.040	0.200 57
0.006		0.005		0.020	
0.0024		0.002		0.010	
				0.004	

TABLE III. Calculated (calc) and experimental (expt) values for the averaged configurational atomic transition energies of Ar (from the $^1S\,3p^6$ state).

Atomic level	T_{expt} (cm^{-1})	T_{calc} (cm^{-1})	Δ (cm^{-1})
4s	94 371.9	94 371.9	0
5s	114 075.6	114 079.1	3.4
6s	120 213.1	120 221.3	8.2
7s	122 940.7	122 948.0	7.3
8s	124 371.5	124 398.6	27.1
4p	106 277.2	106 277.2	0
5p	117 528.1	117 537.1	9
6p	121 690.0	121 715.9	25.9
7p	123 712.0	123 718.6	6.6
3d	113 606.0	113 606.5	0.5
4d	119 713.6	119 656.6	57
5d	122 624.3	122 577.1	47.2
6d	124 228.0	124 161.5	66.5

tegrals for configurations $3p^5nd$ were not involved which means that those dissociations do not present the correct splitting in the present calculation. All the necessary two-electron integrals can be deduced from a few generic integrals namely $\langle 3p_x ns | ns 3p_x \rangle$ for the $3p^5ns$ configurations and $\langle 3p_x np_x | np_x 3p_x \rangle$, $\langle 3p_x np_y | np_y 3p_x \rangle$, $\langle 3p_x np_y | np_x 3p_y \rangle$ for the $3p^5np$ configurations. The radial parts $\Gamma^{(l)}_{\mu\nu,km}(r)$ of the operators of method B were fitted to reproduce those integrals and are listed in Table IV.

D. DIM Ar$_2^+$ data inputs

There is an arbitrariness in the choice of the Ar$_2^+$ data potential values used as inputs in the DIM formalism. Several authors have chosen the *ab initio* POL-CI values of Wadt[49,50] which underestimate the dissociation energy of the $^2\Sigma^+_{u1/2}$ ground state by ~ 0.15 eV. We preferred the LDA values of Michels *et al.*[51] which yield a dissociation energy of 1.34 eV in very good agreement with the experimental values 1.33 eV.[52] The accuracy of the Ar$_2^+$ inputs may of course have significant influence on the final results and one would need very accurate CI *ab initio* or experimental data in a wide distance range. The $\Lambda-\Sigma$ potential curves without spin–orbit coupling were easily determined from the Ω potential curves given in Ref. 17 and the $V^+_\Sigma(R)$, $V^+_\Pi(R)$, $F^+_{\Sigma\Sigma}(R)$, $F^+_{\Pi\Pi}(R)$ could be easily obtained through sums and differences

$$V^+_{\Sigma,\Pi}(R) = \tfrac{1}{2}[E_{^2\Sigma^+_u,\,^2\Pi_g}(R) + E_{^2\Sigma^+_g,\,^2\Pi_u}(R)]$$

and

TABLE IV. Two-electron operators parameters $\Gamma^{(l)}_{\mu\nu,km} = \Sigma_i a_i \exp(-\alpha_i r^2)$.

$\Gamma^{(l)}_{\mu\nu,km}(r)$	a_1	α_1	a_2	α_2
$\Gamma^{(0)}_{xs^*,s^*x}(r)$	0.2200	0.9800	0.0891	0.0184
$\Gamma^{(1)}_{xy^*,y^*x}(r)$	0.0281	0.2607		
$\Gamma^{(1)}_{xx^*,x^*x}(r)$	0.0624	0.2357	0.0002	0.2356
$\Gamma^{(1)}_{xy,y^*x^*}(r)$	0.0113	0.1492		

$$F^+_{\Sigma\Sigma,\Pi\Pi}(R) = \tfrac{1}{2}[E_{^2\Sigma^+_u,\,^2\Pi_g}(R) - E_{^2\Sigma^+_g,\,^2\Pi_u}(R)].$$

Those four pointwise functions were fitted to spline functions in order to get a determination at any geometry. The polarization contribution due to the charged Rg$^+$ ion which appears in the core-polarization pseudopotential of the neutral atoms, was of course not counted twice.

V. CONCLUSION

We have developed a pseudopotential hole-particle Hamiltonian for neutral rare gas excitations allowing to treat the resonance between equivalent degenerate situations where the holes are located on different atoms. For each hole situation, the diagonal term is the sum of the core energy and a one-particle energy. The one-particle contribution is evaluated as the mean value of a one-electron operator involving the kinetic term, the e-Rg$^+$ Coulombic term and the e-Rg and e-Rg$^+$ pseudopotentials, including core-valence polarization potentials. For a given one-particle state, the delocalization of the hole is given by hopping integrals, parametrized from theoretical calculations on Rg$_2^+$ (consistently with DIM methods for Rg$_N^+$). Excitation differences (for a given hole localization) are accounted for by matrix elements of the corresponding one-particle Hamiltonian between determinants which differ though one MO difference. In the final wave functions (after diagonalization of the Hamiltonian), there is no artificial assumption about the respective localization of the hole and the particle, nor about the nature of particle excitations which are only dependent on the extension of the LCAO basis set used to span the excited molecular orbitals. This formalism can be considered as an extension in the short distance range and a generalization of previous model potential methods developed on excimers and exciplexes. The present formulation indeed incorporates the short range resonance and remains valid in the full distance. It can also be viewed as an attempt to develop open-core pseudopotentials. The coupling between the different cores is achieved here via the DIM model to account for core delocalization but one could of course think of different coupling patterns in other physical situations.

The most straightforward application of the present formalism is the study of rare gas dimers. Indeed, the restriction of the explicitly quantal part of the problem to one active electron makes possible the use of a rather large basis set, giving access to more extensive studies of Rydberg states in the full range of internuclear distance and in a wide energy domain. Obviously in the dimer case, the use of a DIM pattern for the core is trivially exact as far as accurate core data are available. Those data can be either fitted on experiments dealing with Rg$_2^+$ valence states. They can also be taken from accurate theoretical studies which require actually further extensive CI calculations, especially on the heavier rare gas ions such as Kr$_2^+$ or Xe$_2^+$. Section II applies the model to the Rydberg states of Ar$_2^*$ providing a test case particularly for checking the pseudopotentials.

Some two-electron intra-atomic contributions have been restored by means of approximations involving projection or operatorial techniques, in order to ensure spatial and spin symmetry as well as a correct dissociation of the molecular states. Spin–orbit coupling for the hole can be introduced in the atom-in-molecules scheme, consistent with the present formalism, since the basis consists of hole-particle excitations with localized holes. Core changes or mixings will thus consistently be taken into account since spin–orbit coupling is treated on the same footing as hole delocalization.

The present formalism is of course not restricted to Rg_2^+ homonuclear dimers. Exciplex systems $(XY)^*$ such as heteronuclear rare gas dimers can easily be treated providing that pseudopotential parameters $e\text{-}X, e\text{-}Y, e\text{-}X^+, e\text{-}Y^+$ are available as well as the XY^+ and X^+Y core data respectively. Of course, there are no more resonance forces, since X^*Y and XY^* situations are no longer degenerate. However, one expects partial core and orbital mixings which the model would provide. Moreover, X^*Y may be accidentally quasidegenerate with XY^{**} as for instance $Ar^*(4s)+Kr$ and $Ar+Kr^{**}(4p)$, due to the coincidence of the atomic excitations respectively.

Of course, one of the most interesting application field concerns excitations in rare gas clusters. One of the issues is to understand how Rydberg excitations develop in the clusters. This involves two aspects: The first one is the extension of hole delocalization in regard of its interaction with the Rydberg electron and the role of screening. The second aspect concerns the spatial spread of the diffuse Rydberg orbitals in an extended cluster which certainly depends on the excitation levels. One may then undertake to understand theoretically the evolution of spectroscopic properties between the atom and the bulk, and the character of exciton peaks observed in experiments (s or p excitations, volume or surface excitons). The same kind of treatment can also be carried on for exciplex systems.

Finally, one may stress that although the rare gases provide very convenient model systems for the study of Rydberg excitations, they are not the only systems exhibiting such properties. Similar models could be extended to all systems in which the unoccupied valence band and the Rydberg band are well separated. Such a situation can be met in saturated carbon chains (alcanes for instance) in which excitations towards the antibonding valence orbitals lie higher than the lowest Rydberg states. A hole basis would then consist of bond-localized σ^* orbitals (the equivalent of np holes in rare gases) and one would need group pseudopotentials to determine the interaction between the Rydberg electron and the localized σ^* band orbitals doubly or singly occupied.

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