Theor Chem Acc (2006) 116: 549–558
DOI 10.1007/s00214-006-0100-x

REGULAR ARTICLE

Gérard Durand · Fernand Spiegelman

Quantum chemistry close to the Fermi level: reducing clusters to few active hole and/or electron systems

Received: 10 December 2004 / Accepted: 11 May 2005 / Published online: 14 March 2006

Abstract Various approximate models to describe the electronic properties of some families of clusters are reviewed. They correspond to specific elementary situations close to the Fermi level where one or few electrons are either removed from (or added to) a closed shell wavefunction. Simple hole-particule excitations are also considered. The models discussed involve diatomics-in-molecules schemes, use of pseudopotential framework extended to replace inert atoms, and finally combinations of both techniques for excited states. Applications to electronic structure of alkaline earth clusters, rare-gas systems or chromophores interacting with rare-gas systems are given also prospects for more complex molecular nanosystems or assemblies.

1 Introduction: warning to the reader

This paper is not a review article but rather a synthesis of some work of our group during these last 20 years, with the scope of illustrating developments in line with some original ideas of Jean-Paul Malrieu and more specially the insight and fun one can get with quantum chemistry models, especially when simplicity becomes successful. We shall try to illustrate here how the analysis provided by Quantum Chemistry can be helpful to design models which prove to be qualitatively and quantitatively efficient in treating specific challenging situations unreachable (in the past when the work was actually initiated or even at the present time) by ab initio methods. Here we will more particularly address examples chosen in the world of clusters, which are interesting and convenient prototypes of complex systems intrinsically characterized by large numbers of atoms and electrons. Complexity is clearly related to the number of electronic and/or nuclear degrees of freedom. However specific clusters with a large number of electrons and atoms can sometimes be simplified into systems with reduced electronic dimensionality. Though a significant part of the work that will be presented hereafter was carried on after Jean Paul Malrieu interrupted his implication in the field of Cluster Physics, one may consider that many of the models were inspired directly by some of his arguments, or at least indirectly by his lessons in electronic structure simplification and modelling. Some of us have certainly learnt much from him in this respect.

There are some families of systems in which the electronic situations of interest differ from ultra-simple closed-shell configurations by the removal of an electron (hole), the addition of an electron (particle) or basic single excitations (hole-particle pairs). In their ground state, neutral rare-gas (Rg) clusters are known to be systems with atomic filled valence shells only interacting via dispersion forces. Actually, their wavefunction can safely be approximated by a single determinant expressed in a delocalized molecular picture:

$$\Phi_0 = \mathcal{A}(\prod_i \phi_{i\alpha}\phi_{i\beta}) \tag{1}$$

where $\mathcal{A}$ is the anstisymmetrization operator, $\phi_{i\alpha}$ are the valence molecular orbitals which are all fully occupied and α and β the spin coordinates.

Equivalently, the same determinant can be expressed in a localized orbital picture:

$$\Phi_0 = \mathcal{A}(\prod_{A\mu} \chi_{A\mu\alpha}\chi_{A\mu\beta}) \tag{2}$$

where A labels the atom and μ the atomic orbitals.

Such a description is also representative of molecular clusters essentially bound by Van der Waals or weak electrostatic forces (A and μ then labels molecules and molecular orbitals respectively).

However, very different electronic situations occur in the case of ionization, electron attachement or excitation. The system is then no longer governed uniquely by the Van der Waals forces, and partial or total electronic delocalization can occur. One has to consider partial electron removal from orbitals lying below the Fermi level, partial electron filling of orbitals above the Fermi level, or both. Obviously, these

G. Durand (✉) · F. Spiegelman
Laboratoire de Physique Quantique, IRSAMC, UMR 5626
Université Paul Sabatier
31062 Toulouse, France
E-mail: gerard.durand@irsamc.ups-tlse.fr

situations can be approached as done in standard quantum chemistry, developing the excitations from the canonical orbitals defined by the Hartree–Fock wavefunction, and achieving a configuration interaction (CI) treatment in a delocalized picture. It can, however, be profitable, since the two representations introduced above are equivalent, to develop the elementary ionization or excitation processes within a representation built from localized solutions for the individual monomers (atoms or molecules). An important precursor contribution to this dual representation was given by Malrieu and Langlet in an early and famous paper [1]. In the present case an ionized state of a rare-gas cluster can be spanned on individual localized holes (for instance with β spin)

$$\Phi_\alpha^+ = \sum_{A\mu} c_{A\mu\beta} a_{A\mu\beta} \Phi_0 \tag{3}$$

$a_{A\mu\beta}$ is the second quantization annihilator of an electron in a spinorbital $\chi_{A\mu\beta}$ on site A.

Obviously such representation can be useful for ab initio calculations held in localized orbitals bases (usually orthogonalized). It turns out to be even more appealing in the perspective of implementing and parametrizing model hamiltonians since the interactions can be readily associated with local situations and hole transfer (and consequently charge transfer) between those localized situations. This is the essence of the diatomics-in-molecules (DIM) [2] models for rare-gas cluster ions, elsewhere also developped under the acronym diatomics in ionic systems (DIIS) [3].

While in rare-gas ionic clusters, a hole is created in the single ground state closed shell determinant, it is also possible to add one or even several electrons. This is the case for instance of non stoichiometric alkali-halide clusters $\mathrm{Na}_n\mathrm{F}_{n-p}$ in which p electrons are to be considered in the field of n Na^+ and $(n-p)$ F^- ions with closed shell structure. The interaction of the excess electrons with the ions can be treated through pseudopotentials. This gives rise to hybrid quantum classical model where the excess electrons are quantal and the ions described by classical coulombic and steric potentials.

Excited states of neutral rare-gas clusters can also be described via simple excitations or electron-hole pairs, namely they can be spanned on combinations of configurations where a single electron is promoted from a localized orbital into an excited one. A straightforward extension of the DIM model for rare-gas ions is to use the following expansion for excited states

$$\Phi^* = \sum_{A\mu\sigma l\zeta} c_{A\mu\sigma l\zeta} a^\dagger_{Al\zeta} a_{A\mu\sigma} \Phi_0 \tag{4}$$

$a^\dagger_{Al\zeta}$ is the second quantization creator of an electron in a spinorbital $\chi_{Al\zeta}$ on site A (here $\mathrm{Ms} = 0$).

Such formulation, which spans the cluster wavefunction on hole and particle states localized on the same center, is similar to the philosophy of excitonic models [4–7]. However the above expansion does not consider the excited orbital relaxation. Furthermore, even the low energy excitations in rare-gas systems are built from Rydberg orbitals which are rather diffuse and actually not necessarily correctly described by localized functions, unlike the hole. In such conditions, it is interesting to built a hole-particle formalism which assumes no constraints with respect to possible delocalization of the excited electron. This is made possible via the use of electron-Rg^+ and electron-Rg pseudopotentials and again the construction of hybrid models combining quantum and classical treatments.

Thus, one can develop via quantum chemistry, descriptions and parametrizations of elementary electronic processes associated with simple quasi-particle operators starting from the Fermi level. The present paper non-exhaustively reviews such techniques and systems that can be treated according to these concepts. Historically, in our group, attempts in this direction were started on the example of s^2 type atom ionic clusters (Mg_n^{+q}, q = 1,2) which are in principle a simple case for charge transfer models. Indeed their atomic constituants have isotropic s valence shells (similar treatments can be achieved on singly charged helium clusters). This is examplified in Sect. 2 which concerns single- or several-hole systems. Extension to heavy rare-gas atoms (Ne, Ar, Kr, Xe) with p valence shells and rare-gas ionic clusters was considered later and is also reported in Sect. 2. Sect. 3 considers the addition of a single or several electrons to a closed shell and reports results obtained on excess-electron alkali halide clusters. Finally Sect. 4 presents a hole-particle formalism combining both possibilities and addressing excitations in rare-gas molecules and clusters. The conclusion indicates possible generalizations of the aspects discussed in the paper.

2 One- and two-hole systems

In the 1980's, interest in clusters boosted this fast growing field both from experimental and theoretical viewpoints. Experimental beam techniques and lasers have made possible obtaining and size-selecting (multi)-charged species that can be investigated using mass spectroscopy. Among various aspects, the Coulomb stability of multi-charged clusters has turned out to be a significant issue in cluster physics [8–18]. In particular, in 1985, an experimental study [8] allowed the observation of an Hg_5^{2+} cluster from electron impact on a beam of mercury clusters. From simple electrostatic considerations, the doubly charged system was expected to break into two singly charged fragments and the existence of stable Hg_n^{2+} clusters appeared surprising. Comparison of the stability in multi-charged clusters with that of nuclei appeared as an interesting challenge. Actually, the structure of Hg_5^{2+} was unknown. Theoretically, ab initio calculations quickly encountered difficulties in dealing with the size of the systems and were hardly practicable at that time for systems with more than four or five atoms.

The DIM treatment of $\mathrm{Hg}_n^{+(+)}$ clusters would have required diatomic data including relativistic effects, which were not available at that time. We decided to treat the isoelectronic problem of Mg clusters [19–21]. The atoms of column II of the periodic table have ground state s^2 configurations and may be considered to keep essentially this ground state structure in small clusters, despite some weak hybridation with the s^1p^1 configuration. The electronic population of a neutral cluster of such elements may thus be seen as a fully filled s orbital band. Following the introduction, the ground state neutral wavefunction is an antisymmetric product of occupied atomic orbitals of spin α and β as defined in Eq. (2). The basic idea was to treat the positive ion as a single hole problem delocalized on the different sites of the cluster through a single-hole operator. For Mg_n^+, we consider n basis functions $\Phi^+_{A\alpha}$ with spin projection Ms = +1/2, each one describing a hole localized on a single atom (A)

$$\Phi^+_{A\alpha} = a_{As\beta}\Phi_0, \tag{5}$$

where $a_{As\beta}$ is the hole-creation operator in a 3s atomic orbital with spin β on atom A. The wavefunction of the cluster is a linear combination of the $\Phi^+_{A\alpha}$'s and the model hamiltonian is a $n \times n$ matrix. The diagonal terms of the hamiltonian describe the energy of a localized hole in the field of the other neutral atoms. It includes the interactions between the positive atom A and the neutral atoms $B(V^+_{AB})$ and the neutral-neutral interactions (V_{BC}). The off-diagonal terms of the Hamiltonian are hopping integrals between atoms A and $B(F^+_{AB})$. V_{AB} is the ground state Van der Waals energy of the neutral Mg_2 dimer [22,23]. V^+_{AB} and F^+_{AB} can be deduced from the potential curves of Mg_2^+ [4].

The model was then extended to doubly charged clusters, considered as two-hole systems in the s band. In this case we defined n^2 localized Valence Bond wave functions

$$\Phi^{++}_{AB\zeta\sigma} = a_{As\zeta}a_{Bs\sigma}\Phi_0 \tag{6}$$

with (ζ, $\sigma = \alpha$ or β) and the doubly charged clusters were treated like two-hole systems, including correlation. The model hamiltonian is a $n^2 \times n^2$ matrix. The configuration basis involves situations characterized by either two holes on the same atom, or holes on different atoms. The diagonal elements involve two additional interactions, namely the coulombic repulsion V^{++}_{AB} between holes on different atoms A and B, and the interaction V^{2+}_{AC} between a doubly charged site Mg^{++} and a neutral Mg atom C. In addition to the Mg–Mg^+ hole hopping, one has to consider the jump F^{2+}_{AB} of an hole between a doubly charged atom and a neutral one. Again, these can be deduced from ab initio CI calculations on Mg_2^{++} [24]. The Hamiltonian depends only on the interatomic distances and is isotropic. One may add to this basic model polarization contributions which bring three-body effects since the electric field on each site is caused by vector addition of the fields induced by two localized charges. This means treating one or two active holes in a polarizable s band. The method is identical to a DIM procedure with the inclusion of polarization forces. However, this involves static and dynamical polarization (meaning here the interaction between properly polarized localized hole-configurations).

One of the early results was the evidence in the case of Mg_4^+ of a competition between two isomers differing strongly in the extent of the hole (or charge) delocalization. This problem allowed us to study the conflict between hole delocalization (kinetic energy stabilization) versus hole localization stabilized by polarization forces [25]. The inclusion of dynamical polarization effects was shown to be quantitatively important to obtain relevant ionization potentials and qualitatively important to determine correctly the balance between delocalization and polarization effects, this balance being distorted in SCF treatments in favor of hole-concentrating structures.

The main result concerns the stability of the doubly charged clusters versus the coulomb explosion. Our calculations showed that these clusters are metastable with fission barriers of a few tenth of an eV. For a given n value, Mg_n^+ and Mg_n^{++} very often have similar geometries, these latter being quite different from those of the neutral species. As a consequence, vertical ionization from Mg_n^+ could result in a long-lived doubly-charged cluster ion whereas a vertical double ionization of the neutral Mg_n cluster would yield conformational highly excited species with short life time (see Fig. 1). Such an analysis was confirmed four years later in the framework of pseudopotential local-spin-density calculations [26] and is nowadays accepted [9].

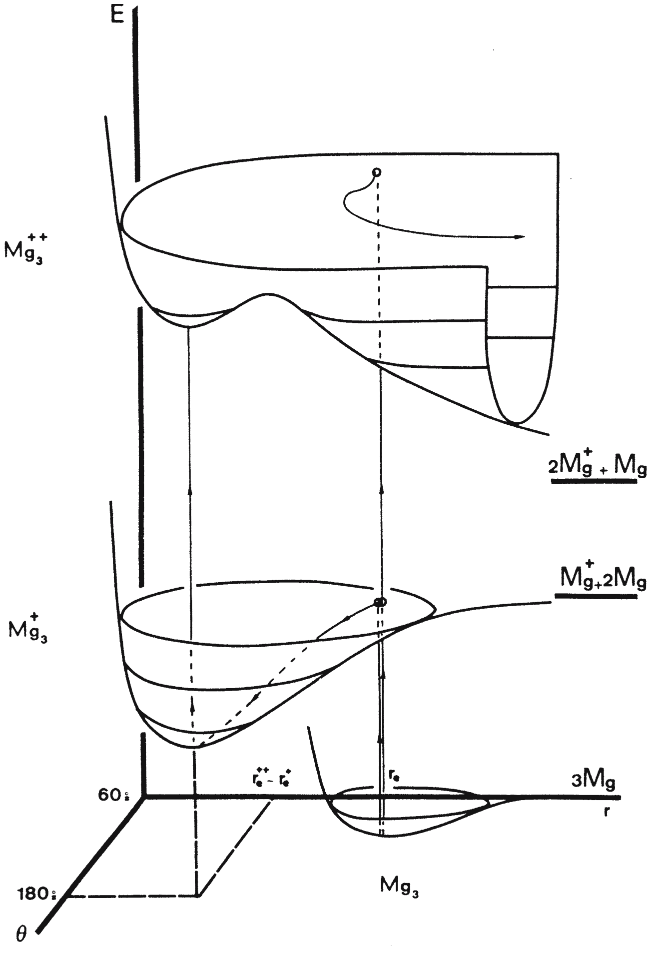

Fig. 1 Schematic view of the potential energy surfaces of Mg_3^{q+}, $q = 0, 1, 2$ showing how long lived metastable Mg_n^{2+} clusters could be obtained (after [19]).

The same methodology can be applied to the case of cationic rare-gas clusters. The model for helium is isomorphic to that developed for magnesium [27]. For the heavier rare gases, the hole can be made in either one of the three degenerate atomic p shells. A main difference with the previous clusters therefore lies in the anisotropy of the interactions. The lowest ion states only involve ionization of the p band (on atomic xenon, the ionisation potential of the s band is 21.2 eV, higher by 9.1 eV than the first IP=12.1 eV). Configurations corresponding to s electron ionization can be safely neglected. The wave function of the cluster is now a linear combination of the 3n functions (5) (n is the size of the cluster):

$$\Phi^+_{A\alpha} = a_{A\mu\beta}\Phi_0, \tag{7}$$

where $a_{A\mu\beta}$ is the hole-creation operator in a p_μ ($\mu = x, y, or\ z$) atomic orbital of spin β on atom A. For Rg_2^+ the symmetry results in a partition of the Hamiltonian into a Σ block (holes in the z-directed σ atomic orbitals) and two degenerated Π blocks. Then we defined two potentials V^+_σ and V^+_π, respectively associated with interactions between a neutral atom and an ionized one, the electron being removed from either orbital $3p_\sigma$ or $3p_\pi$. Similarly, one has two hopping integrals F^+_σ and F^+_π. For the general n-atom cluster, hopping integrals can be supposed to be transferable from the diatomic problem, with some local rotations. The spin-orbit contributions can be included according the semiempirical scheme proposed by Cohen and Schneider [28,29] resulting in a coupling of the Σ and Π parts and in a $6n \times 6n$ matrix for the Hamiltonian. Polarization contributions can also be added whenever the atomic polarizabilities are large, as well as the interactions between induced dipoles.

This non-empirical model hamiltonian has been applied to Xe_n^+ clusters [30,31]. The main and most significant result concerns a systematic view of how these ionic clusters are constructed. Since the pionneering work of Haberland [32], cationic rare-gas clusters were supposed to build only around dimer cores. This was in line with the assumption that exciton propagation in rare-gas matrices was mediated by dimers and with the relatively large stability of Xe_2^+. Actually, due to the p nature of the valence atomic orbitals, the hole delocalization proceeds along one direction but it rapidly becomes less favourable to extend the delocalization of the hole on to an extra nth atom than to polarize a neutral atom located in a crown around a $(n-1)$-atom linear cluster. Surprisingly, larger units for charge delocalization were found: linear charged clusters Xe_3^+ and Xe_4^+ (cores) generate two families obtained by arranging neutral atoms stabilized by polarization forces in crowns around the cores. Each crown may bear up to five atoms yielding two crowns around Xe_3^+ and three around Xe_4^+. The 13 and 19 cationic rare-gas clusters thus appear to have compact structures with two and three filled crowns, respectively (see Fig. 2). This result was found independently by Kuntz [2] on Ar_n^+ with a DIM method (but without spin-orbit coupling and without induced dipole-dipole terms) and confirmed by subsequent ab initio multi-reference CI calculations [33] (see also the recent DIM work of Paska et al. [34] on Xe_n^+). A remarkable feature is that the main magic numbers for the ions and the neutrals are the same ($n = 13$ and 19) although due to different reasons: whereas the structures of the neutrals mainly result from the arrangements of shells of atoms with no delocalization at all, the ions are characterized by inhomogenous electronic structure in the core and in the external atoms. A signature of this anisotropy is the inequivalent Rg–Rg nearest–neighbor distances observed in the cores and in the outer shells, unlike in the neutral where all Rg–Rg distances are essentially equivalent.

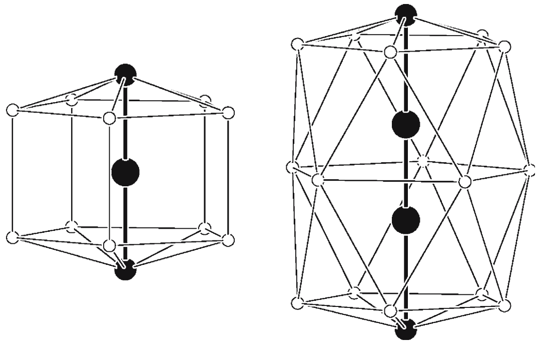

Fig. 2 Xe_{13}^+ and Xe_{19}^+ optimal structures illustrating the complete filling of pentagonal crowns with neutral Xe atoms around Xe_3^+ and Xe_4^+ respectively. *Empty circles* neutral rare-gas atoms. *Black circles* charged rare-gas atoms (size proportional to charge)

One attractive feature of the DIM model or its extensions is that it requires low computing effort and can thus be implemented in molecular dynamics simulations. This advantage was extensively used to simulate absorption spectra recorded in several experimental groups. Simulation of absorption spectra can be either achieved in the framework of molecular dynamics simulations or classical Monte–Carlo schemes. This was first attempted in the present context on Ar_3^+ [35] using classical molecular dynamics. Later, fully quantum simulations were achieved on the trimer [36], and finally simulations on larger Ar_n^+ clusters were carried on [37–39]. Simulations on the heavier clusters Xe_n^+ including spin-orbit coupling were recently achieved by Kalus and Hrivňák [40], using the diatomics potential curves of Paidarová and Gadéa [41] to simulate the absorption spectra of Xe_n^+, experimentally recorded by Haberland et al. [42].

We show here an illustration (see Fig. 3) of similar simulations achieved in the canonical ensemble using Monte-Carlo simulations (F. Spiegelman, unpublished results) at T=100 K (however constructed from slightly different diatomic pairs [43]) yielding results in close agreement with the work of Kalus and Hrivňák.

Figure 4 shows the histograms of the distribution of distances obtained along the simulation. It is seen both on Xe_{13}^+ and Xe_{19}^+ that the intra-core distances have smaller fluctuations than the distances between core atoms and those belonging to the neutral crowns (core–neutral) or the distances between the neutrals (neutral–neutral). The fluctuation of the charges during the simulation confirms the picture of an ionic core surrounded with neutrals shells, as seen in Table 1.

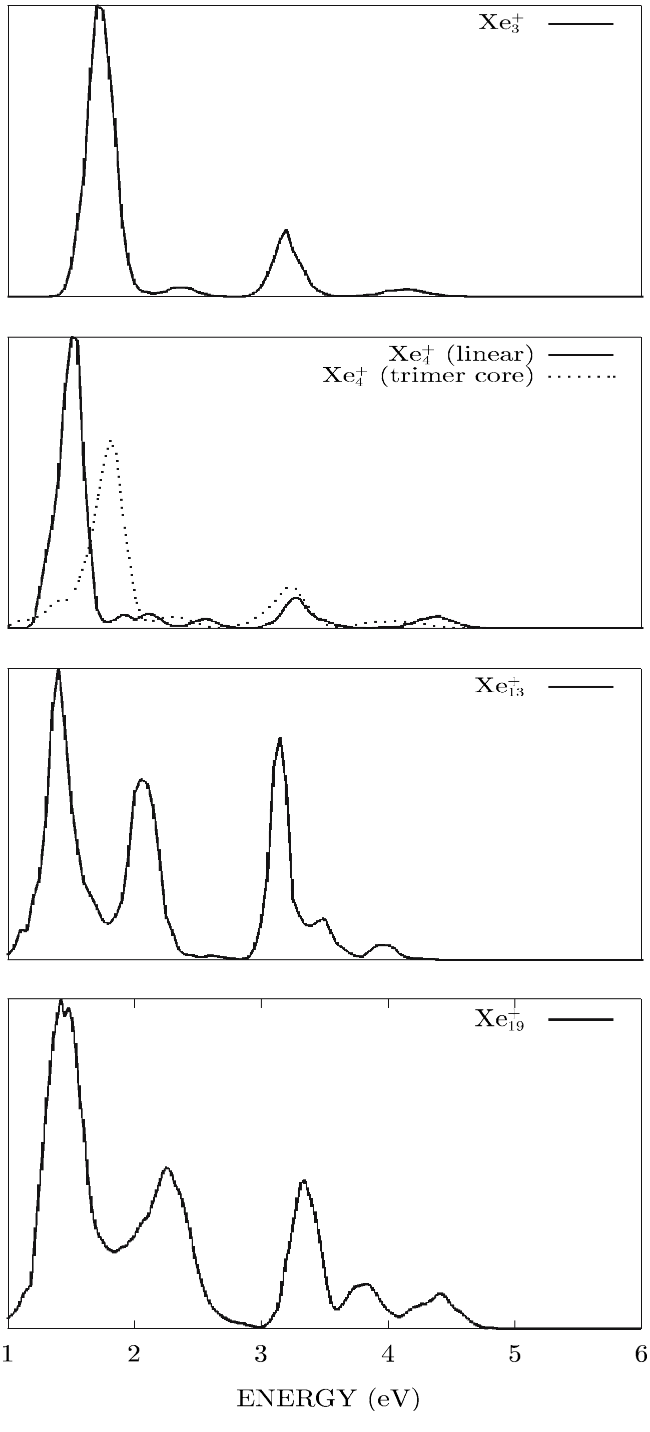

Fig. 3 Classical Monte–Carlo determination of absorption spectra of selected Xe_n^+ clusters at temperature $T = 100\,K$

3 Systems with few active electrons

Other clusters or molecular systems result from the addition of a single electron to a closed shell system. A simple example is provided by electron attachement to rare gases. The attachement of weakly bound electron to closed shell molecules is presently an important field at the interface between physics and biology [44–46]. One difficulty which arises when adding an electron, is that localization is by far less obvious than when creating holes. The added electron can actually be strongly delocalized in the lowest unoccupied molecular orbital of the neutral system self-consistently relaxed. Such interaction governs for instance the weak electron affinity of dipole-bound states where an electron is bound thanks to the field of a dipolar molecule. Polarization of the neutral part and its correlation with the external electron can be large. In rare gases, the bonding is solely due to polarization and correlation.

An appealing tool to model such states, not necessarily localized, is to use hybrid descriptions, treating the neutral part classically and the external electron (s) via model potentials or pseudopotentials, possibly supplemented by core polarization operators to include the response of the classical part to the fluctuation of the external one, similarly to the so-called core-polarization in atoms.

An example of single-electron systems is provided by non-stoichiometric alkali halide clusters, M_nX_{n-1}, which can be considered as single electron attached to $n\,M^+$ and $(n-1)\,X^-$ ions. The total hamiltonian is written as the sum of a quantum term for the electron and of a classical part for the ion–ion pairs contributions. This classical part is the sum of two terms the repulsion U_{rep} between the M^+ and X^- ions (sum of Born–Mayer terms) and of the sum U_{coul} of the coulombic interactions between these ions. The quantum hamiltonian of the electron in the field of the ions

$$h = -\frac{\Delta}{2} + \sum_M \left(-\frac{1}{r_M} + W_M \right) \sum_X \left(\frac{1}{r_X} + W_X \right) \tag{8}$$

is a one-electron operator including the standard coulombic interactions of the electrons with the ions together with effective interactions via the W_M and W_X pseudopotentials. These may also include effective core-polarization pseudopotentials which account for the static and dynamical core polarizabilities as in the formalism first derived by Müller and Meyer [47]. Full charge transfer (charges ± 1 on the ions) has been widely used in simulations dealing with stoichiometric alkali–halide clusters even for large alkali atoms like cesium [48]. This model, so-called the "rigid ion model", can be complemented by polarization terms and dipole–dipole terms [49], yielding the so-called "polarizable ion model". The latter was shown to provide results in fair agreement with ab initio calculations on alkali-halide clusters [50]. For this family of clusters, charge transfer is supposed to increase in the bulk limit. The one-electron model has been applied to Na_nF_{n-1} clusters [51,52] and successfully compared with extensive CI calculations [53]. In this NaF case, charge transfer, even in the case of diatomics, is almost fully completed. Though the atomic charge is not an observable and should be taken cautiously from ab-initio calculations, we report here the NaF natural population analysis, 0.99 and 0.98 from Hartree–Fock and MP2 calculations respectively. Similarly, a Hartree-Fock calculation on Na_4F_4 provides a charge transfer of 0.98 (F. Spiegelman and G. Durand,

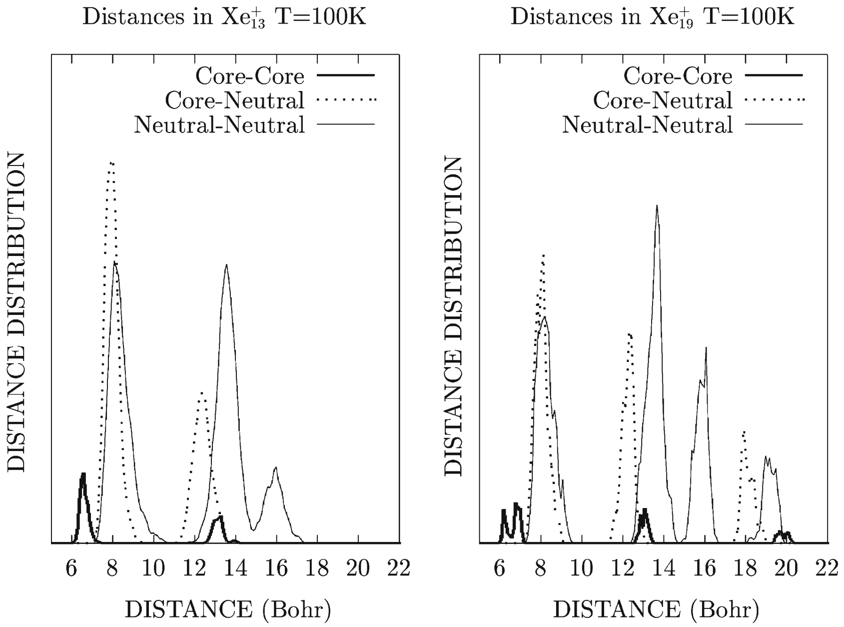

Fig. 4 Classical Monte–Carlo simulation of the distance distributions in selected Xe_n^+ clusters at temperature $T = 100\,K$

Table 1 Averaged charge populations on core atoms of singly charged rare-gas clusters with either trimer or tetramer core during a classical Monte–Carlo simulation at temperature T=100 K.

cluster	averaged charges			
Xe_3^+	0.24	0.52	0.24	
Xe_4^+(linear)	0.08	0.42	0.42	0.08
Xe_{13}^+	0.16	0.61	0.19	
Xe_{19}^+	0.04	0.45	0.43	0.03
Ar_3^+	0.23	0.52	0.24	
Ar_4^+(linear)	0.10	0.39	0.40	0.11

unpublished results). Such a hybrid model with a single electron makes possible the investigation of clusters up to a few tens of atoms within exhaustive simulations, either concerned with structural optimization via global algorithms, isomerization, thermodynamics, or dynamical determination of optical properties.

Whereas the model does not make any hypothesis upon localization, typical localization sites (weaker or stronger) can be listed. The electron may localize on a pending sodium (Na-tail), on a Na-apex (surface state) or in a vacancy (F-center), as shown in Fig. 5. The systematic exploration of structures up to $n = 29$ clusters allowed us to propose new localization sites. For instance $Na_{23}F_{22}$ (Fig. 5) is characterized by the absence of a NaF_2 subunit or by a partially depopulated face [54]. The main success of the model concerns the reproduction of the experimental ionization potentials [51] and of the photoelectron spectra [52]. Examples of F-center versus Na-tail cluster absorption spectra are shown in Fig. 6. As well on Na_4F_3 and on Na_7F_6 two experimental techniques, resonant two photon ionization (R2PI) and depletion spectroscopy, are needed to obtain the whole theoretical spectrum. This is the sign of predissociation of excited states as we showed in the case of the Na_5F_4 cluster [55].

Moreover this modelling of the cluster into a single electron system provides a convenient support for excited states dynamics and the interpretation of pump–probe experiments [56]. Excited state dynamics of Na_2F could be investigated via quantum wave packet propagation [57] on the potential energy surfaces calculated with the above mentioned method. The vibrational motion of Na_2F after femtosecond excitation in the lowest excited state was assigned to the dominant bending motion [56]. However a centrifugal type coupling with the symmetric stretch motions of F–Na–F was shown to be responsable for a beating-time dynamical behavior.

Note that the single electron model can be extended to treat M_nX_{n-p} clusters with p excess electrons. Correlation of the p excess electrons must obviously be included via CI (possibly DFT). The required cost is anyway less than full-electron calculations, or even standard valence pseudopotential or frozen core calculations. Electronic excited states of such two-electron cluster, namely Na_3F were recently investigated [58,59] with this two-electron version (achieving full CI for the two electrons) in order to interpret recent pump-probe experiments where the short-time dynamics of the excited states was recorded [60].

Another important extension corresponding to the interaction of chromophores with electronically inert molecules, clusters or matrices is to be mentioned. Such situation occurs in molecular clusters, in inert solvants or in the case of trapped molecules in cryogenic matrices. In theoretical investigation, these systems often receive a DIM type treatment [61–66]. This is fairly reasonable for the ground state, the valence excited states or even possibly the lowest non-valence states (charge transfer and zwitterionic states). However, the application of DIM is more questionable for higher states like Rydberg ones where the electron may be diffuse and delocalized and therefore not easily spanned by the usual

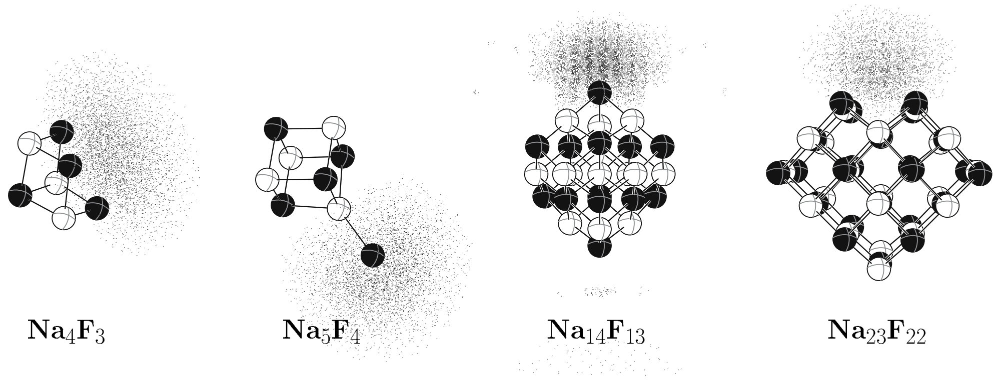

Fig. 5 Localization of the electron in the four principal kinds of Na_NF_{n-1} structures: F-center (Na_4F_3), Na-tail (Na_5F_4), localized surface state ($Na_{14}F_{13}$), and edge-state ($Na_{23}F_{22}$)

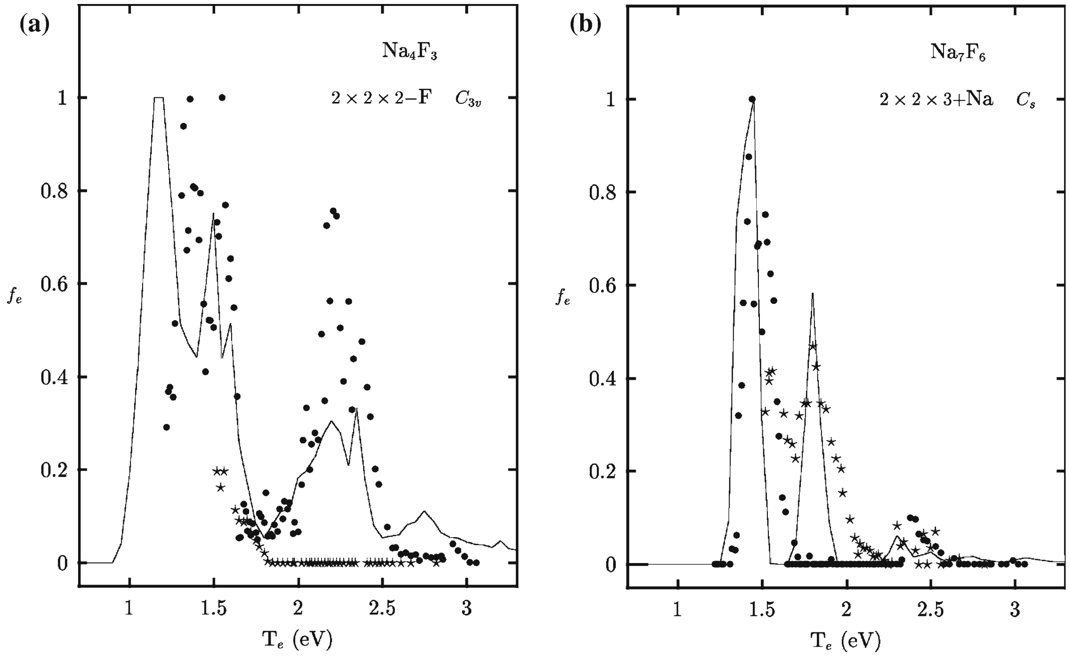

Fig. 6 Example of spectra of F-center cluster (*a*) and of Na-tail (*b*) cluster. Comparisons between theoretical results (*solid line*) and experimental R2PI (*dots*) and depletion (*stars*) spectra.

DIM representation. For instance, a number of investigations were dedicated to spectroscopic studies of alkali atoms in rare-gas matrices [67,70] or clusters [71] concerned with the lowest states ($3s$ and $3p$ in sodium). In clusters, higher excited states (such as $4s$ and $4p$ which are already Rydberg states) may be of interest. They correspond to an electron surrounding an ionized cluster core and can hardly be described in terms of matrix elements involving pair potential only [72,73]. However more sophisticated treatment can be defined. Indeed one again can benefit from the fact that the orbitals of the active electrons involved in the excitation process are restricted to those of the chromophore (excitation from chromophore HOMO's towards chromophore's virtual orbitals). Here again, hybrid descriptions can be used with the help of extended pseudopotentials. In the case of a chromophore in interaction with a rare gas system, for instance, pseudopotentials can be derived to model the interaction of the active chromophore electrons with the rare-gas atoms (Rg). A hybrid model can then be constructed, where the chromophore is treated explicitly by means of standard methods while the interaction of the chromophore electrons with the rare gas atoms are described via these inert atom pseudopotentials, eventually non local, and finally the interactions among rare-gas atoms U_{Rg-Rg} are taken into account classically as well as those of the chromophore core ions with the rare-gas atoms $U_{\text{core}-\text{Rg}}$

$$H = \sum_{i}^{\text{act}} -\frac{\Delta_i}{2} + \sum_{A}^{\text{act}} \left(-\frac{z_A*}{r_{iA}} + W_A(i)\right) + \sum_{i<j}^{\text{act}} \frac{1}{r_{ij}} + \sum_{i}^{\text{act}} \sum_{B}^{\text{inert}} W_B^{Rg}(i) + U_{\text{core}-Rg} + U_{Rg-Rg}. \tag{9}$$

Such a scheme establishes an active/passive partition between the chromophore and the rare-gas system, very parallel to the standard partition between atomic core and valence electrons, which is the essence of the usual pseudopotential method. Polarization operators can obviously be used to restore the response of the inert atoms to the valence situation. Such scheme, which extends early model potential descriptions on diatomics, was improved by defining nonlocal inert atom pseudopotential and used to investigate the electronic structure of alkali atoms in interaction with rare-gas atoms, molecules and clusters. It can also be very efficient in the description of chromophore trapped in inert matrices, providing access to high electronic states [74–76].

4 Hole-particle systems

So far, we have described situations resulting either from hole creation, or from electron addition to closed shell systems, separately. Both can be combined to study excitations. This is the case for instance in excitation occuring in pure rare-gas systems in which a hole is made in the valence shell and excitation takes place in a diffuse orbital. Rare-gas clusters have very large HOMO–LUMO gaps, the lowest excitations occuring in the VUV range. In atoms, the lowest excited orbitals are already diffuse and are often characterized as the lowest members of Rydberg series converging to the ion limits. The same occurs for diatomic molecules, which constitute excimer and exciplex systems and which motivated numerous studies in the 1970's due to their possible use as laser sources in the VUV range. Again, their excited states can roughly be considered as Rydberg series converging towards the diatomics ion states, which govern their stability. For instance the electronic structure in Ar_2^* can be qualitatively understood as resulting essentially from the interplay of Rydberg series associated with four ion parents states, namely $^2\Sigma_u$ (bound by 1 eV), $^2\Pi_g$ (moderately bound), $^2\Pi_u$ (non-bonding) and $^2\Sigma_g^+$ (repulsive), shifted to the various relevant atomic neutral asymptotes. In Xe_2^*, the situation is complexified by the important spin-orbit coupling which has the same order of magnitude as the valence binding of the lowest ion state.

As mentioned in the introduction, the crudest way to deal with excitations is to use a DIM method built on electron-hole configurations based on the various atoms. Such a model was actually derived by Last and George [4] to deal with 3s excitations in argon clusters. However, such approach may face several difficulties. The first one is that one obviously needs diatomic data, which are not always available. Moreover, as mentioned above, couplings occur between various excited configurations. This is true even for the repulsive states correlated to the lowest atomic excited levels, which interact with attractive states associated with higher asymptotic levels. DIM models should then be defined within a multi-excitation scheme. Its definition should then rely on diabatic descriptions. Such developments are in any case far less straightforward. Finally, another problem lies in the expression of a diffuse excited orbital as a non-relaxed combination of purely local configurations, unless again higher excited states are taken into account in the DIM scheme.

An alternative approach is to use different schemes for holes and particles. Such a hybrid description [77] was proposed to investigate the electronic structure of excited rare-gas molecules and clusters. It is based on pseudopotentials. The idea is to define basis configurations corresponding to the interaction of the Rydberg electron with one Rg^+ atom and with $(n-1)$ Rg neutral atoms. These interactions are respectively simulated by e-Rg^+ and e-Rg one-electron pseudopotentials. The total wavefunction is then a combination of those configurations where the hole is supposed to be localized on atomic sites and the particle (Rydberg electron) is not constrained.

Starting from the neutral van der Waals ground state Φ_0 as defined by Eq. (2), the hole-particle basis is defined as

$$\Phi^{i\sigma}_{A\mu\tau} = a^{\dagger}_{i\sigma} a_{A\mu\tau} \Phi_0, \qquad (10)$$

where $a^{\dagger}_{i\sigma} a_{A\mu\tau}$ is the promotion operator of an electron from spin-orbital $\chi_{A\mu\tau}$ localized on atom A into a Rydberg spin-orbital $\phi_{i\sigma}$.

The main assumption is the use of basis configurations relying on separate descriptions of the contributions due to the core and of those due to the excited electron. The diagonal elements of the Hamiltonian are sums of a core term, $E_{A\mu\tau}$ representing the energy of a Rg_n^+ ion (see above) with a localized hole in spin-orbital $\chi_{A\mu\tau}$ and of an electron contribution representing the energy of an electron in a spin-orbital $\phi_{i\sigma}$ interacting with the Rg^+ atomic ion and the $(n-1)$ Rg neutral atoms. The electronic contribution can be calculated as the expectation value of a single-electron hamiltonian via e-Rg^+ and e-Rg pseudopotentials

$$\begin{aligned} H^{i\sigma i\sigma}_{A\mu\tau A\mu\tau} &= E_{A\mu\tau}(Rg_n^+) + <\phi_{i\sigma}| - \frac{\Delta}{2} - \frac{1}{r_{Rg^+}} \\ &\quad + W_A^{Rg^+} + \sum_{B\neq A}^{Rg} W_B^{Rg} |\phi_{i\sigma}> . \end{aligned} \qquad (11)$$

The static polarization of the Rg and Rg^+ cores in the presence of the Rydberg electron and the Rydberg-core correlation can be included by means of core-polarization pseudopotentials. The off-diagonal terms of the hamiltonian represent the couplings between these basis configurations. The most important off-diagonal elements are those between states with a single orbital difference, namely hole hopping functions (coupling hole-particle states which differ through the location and the possible orientations of the holes)

$$H^{i\sigma i\sigma}_{A\mu\tau B\nu\tau} = F_{\mu\nu}(R_{AB}) \qquad (12)$$

and excitation transfer (coupling states with the same hole but different particle spin-orbitals)

$$\begin{aligned} H^{i\sigma j\sigma}_{A\mu\tau A\mu\tau} &= <\phi_{i\sigma}| - \frac{\Delta}{2} - \frac{1}{r_A} \\ &\quad + W_A^{Rg^+} + \sum_{B\neq A}^{Rg} W_B^{Rg} |\phi_{j\sigma}> . \end{aligned} \qquad (13)$$

Such a model has been applied to Ar_2^* [78] and Xe_2^* [79] (including spin-orbit coupling). For these excimer molecules, transferability to high excited states was demonstrated: the model was shown to reproduce a wide pannel of experimental spectroscopic data. It also proved its efficiency to theoretically investigate excited states in an energy range that ab initio methods can hardly yet address, even at the present time. The absorption spectra of small argon clusters in the range $n = 3 - 13$ could also be investigated [80].

5 Conclusion

Electronic structure calculations and molecular modelling has gained a huge benefit from the incredible progress of computing hardware. Methodological and software progress are also fastly developing. The explicitely correlated methods of quantum chemistry (coupled cluster methods, Perturbation theory or multi-reference schemes) are powerful and can in principle address any situation, including weak bonds, excited states. Their convergency is however slow with regard to the atomic basis set extension and also as a function of the CI expansion, unless special formalisms are used [81,82]. As a consequence, they are usually limited to sytems with a relatively small number of electrons. Density functional methods are applicable to larger systems and are now widely used to address clusters, nanosystems or biomolecules, especially within the efficient Car–Parinello scheme. No doubt that both types of methods will still be made more efficient via for instance linear-scaling techniques. However fundamental problems also remain to be addressed: more accurate and general functionals remain to be found, within density functional theory in particular, in order to safely treat weak bonding situations and especially dispersion forces. Despite the growing success of time-dependant density functional theory, the treatment of excited states still deserves further theoretical developments.

Therefore, and despite the progress of combined ab initio electronic structure/molecular dynamics methods, the development of models with various complexities (involving mixed quantum-classical description) remains a long-term activity to obtain useful potential energy surfaces of large systems, especially whenever excited states are concerned. This becomes essential if one wants to investigate dynamical and thermodynamical aspects such as collision, fragmentation, reactivity or dynamical behaviour of systems, which require “on-the fly” calculations. There is obviously a price to pay: the conception of the models depends on the systems or at least on the families of systems addressed. This offers less generality than ab initio methods when applicable. Clearly the routes of modelling and ab initio calculations should never be considered as independant. On the contrary, they should cross rather often, and sometimes be combined: Ab initio calculations are needed to analyze, understand, design and relevantly parametrize the models. They are also needed to achieve a-posteriori checks. Mixed models require skills with both techniques.

The non-exhaustive cases that were briefly summarized in this paper involve modelling of exited states and go beyond the domain addressed by ground state force fields. Though they are actually concerned with specific situations and systems, the concepts and methods can nevertheless be extended to apparently much more complex systems. Electronic and structural properties of singly charged aromatic molecule assemblies were found to present charge delocalization on small subunits [5,6], very close to that found for pure rare-gas ion clusters. Thus, provided that molecular anisotropy is incorporated, the same models can be used for simple atom clusters or assemblies involving rather large molecules.

Transport properties, in single-dimension conducting nanostructures based on molecules, can be investigated considering band structure, but also in terms of charge resonance in one-dimension [83]. Excitation transfer in biomolecules [7] is also an extremely interesting field and could be treated, including the real time-aspects, by combining excitonic descriptions and well grounded ab initio data on the constituant amino-acid monomers. Extension of pseudopotential methods beyond the standard limits as done on inert rare-gas atoms, could also be worked on to describe the interaction of an electron with a full molecule, as previously mentioned in the cases of weakly bound electrons. This would allow mixed quantum-classical treatments of reactivity in solvants (see for instance Borgis et al. [84]). The challenge is now also to efficiently combine those electronic structure models with large scale molecular dynamics simulations, and more precisely in the case of excited states, non adiabatic dynamics.

References

1. Langlet J, Malrieu J-P (1976) Localization and local phenomena in molecular excited and ionized stationary states. In: Chalvet O, Daudel R, Diner S, Malrieu J-P (eds) Localization and delocalization in quantum chemistry, vol II. Reidel Publishing Company, Dordrecht, Netherlands. pp 15–47
2. Kuntz PJ, Valldorf J (1988) Z Phys D 8:195
3. Last I, George TF (1990) J Chem Phys 93:8925
4. Last I, George TF (1993) J Chem Phys 98:6406
5. Bouvier B, Brenner V, Millié P, Soudan J-M (2002) J Phys Chem A106:10326
6. Bouvier B, Millié P, Mons M (2004) J Phys Chem A108:4254
7. Bouvier B, Gustavsson T, Markovitsi T, Millié P, (2002) Chem Phys 275:75
8. Bréchignac C, Broyer M, Cahuzac Ph, Delacretaz G, Labastie P, Wöste L (1985) Chem Phys Lett 118:174
9. Echt O, Märk TD (1994) Multiply charged clusters. In: Haberland H (ed) Clusters of atoms and molecules II : solvation and chemistry of free clusters, and embedded, supported, and compressed clusters, Springer Series in Chemical Physics, vol 56, Springer, Berlin Heidelberg New york. p 183
10. Lang B, Vierheilig A, Wiedenmann E, Buchenau H, Gerber G (1997) Z Phys D Atoms Mol Clusters 40:1
11. Bescos B, Lang B, Weiner J, Weiss V, Wiedenmann E, Gerber G, (1999) Eur Phys J D 9:399
12. Calvayrac F, Reinhard PG, Suraud E (1999) Eur Phys J D 9:389
13. Scheier P, Dunser B, Senn G, Drexel H, Winter HP, Aumayr F, Betz G, Biasioli F, Fiegele T, Mark TD (1999) Eur Phys J D 9:91
14. Brechignac C, Cahuzac P, Concina B, Leygnier J (2001) Eur Phys J D 16:91
15. Herlert A, Schweikhard L, Vogel M (2001) Eur Phys JD 16:65

16. Teuber S, Doppner T, Fennel T, Tiggesbaumker J, Meiwes-Broer KH (2001) Eur Phys J D 16:59
17. Ntamack GE, Chandezon F, Manil B, Lebius H, Tomita S, Guet C, Njock MGK, Huber BA (2003) Eur Phys J D 24:153
18. Schweikhard L, Hansen K, Herlert A, Marx G, Vogel M (2003) Eur Phys J D 24:137
19. Durand G, Daudey J-P, Malrieu J-P (1986) J Physique 47:1335
20. Durand G, Daudey J-P, Malrieu J-P (1987) Lecture Notes in physics, vol 269. Springer Berlin, Heidelberg New York pp 127–134
21. Durand G (1989) J Chem Phys 91:6225
22. Huber KP, Herzberg G (1979) Constants of diatomic molecules. Van Nostrand, New York
23. Scheingraber H, Vidal CR (1977) J Chem Phys 66:3694
24. Durand G, Spiegelmann F, Bernier A (1987) J Phys B 20:1161
25. Durand G, Daudey J-P, Malrieu J-P (1988) Theor Chim Acta 74:299
26. Reuse F, Khanna SN, de Coulon V, Buttet J (1990) Phys Rev B 41:11753
27. Seong J, Janda KC, Halberstadt N, Spiegelmann F (1998) J Chem Phys 109:10873
28. Cohen JS, Schneider BJ (1974) J Chem Phys 61:3230
29. Schneider BJ, Cohen JS (1974) ibid 61:3240
30. Amarouche M, Durand G, Malrieu J-P (1988) J Chem Phys 88:1010
31. Amarouche M, Durand G, Malrieu J-P (1988) Z Phys D 8:289
32. Haberland H (1985) Surf Sci 156:305
33. Böhmer H-V, Peyerimhoff SD (1989) Z Phys D 11:239
34. Paška P, Hrivňák D, Kalus R (2003) Chem Phys 286:237
35. Amarouche M, Gadéa FX, Durup J (1989) Chem Phys 130:145
36. Gadéa FX, Le Quéré F (1995) J Chem Phys 102:7830
37. Grigorov M, Spiegelmann F (1996) Surf Rev Lett 3:211
38. Galindez J, Calvo F, Paska P, Hrivnak D, Kalus R, Gadea FX (2002) Comp Phys Comm 145:126
39. Calvo F, Galindez J, Gadea FX (2003) Phys Chem Chem Phys 5:321
40. Kalus R, Hrivňák D (2002) Chem Phys 278:21
41. Paidarová I, Gadéa FX (2001) Chem Phys 274:1
42. Haberland H, van Issendorf B, Kolar T, Kornmeier H, Ludewigt C, Risch A (1991) Phys Rev Lett 67:3290
43. Daskalopoulou M, Böhmer HU, Peyerimhoff SD (1990) Z Phys D Atoms Molecules and Clusters 15:161
44. Desfrançois C, Abdoul-Carime H, Schultz CP, Schermann J-P (1995) Science 269:1707
45. Desfrançois C, Carles S, Schermann J-P (2000) Chem Rev 100:3943
46. Lecomte F, Schermann J-P, Desfrançois C (2002) Multipole-bound anions of organic molecules. In: Kalcher J (ed) Theoretical prospect of negative ions, Research sign post pp 29-41
47. Müller W, Meyer W (1984) J Chem Phys 80:3311
48. Diefenbach J, Martin TP (1985) J Chem Phys 83:4585
49. Phillips NG, Conover CWS, Bloomfield LA (1991) J Chem Phys 94:4980
50. Aguado A, Ayuela A, Lopez JM, Alonso JA (1997) J Phys Chem B 101:5944
51. Durand G, Giraud-Girard J, Maynau D, Spiegelmann F, Calvo F (1999) J Chem Phys 110:7871
52. Durand G, Spiegelmann F, Poncharal Ph, Labastie P, L'Hermite J-M, Sence M (1999) J Chem Phys 110:7884
53. Bonačić-Koutecký V, Pittner J, Koutecký J (1996) Chem Phys 210:313
54. Durand G, Spiegelmann F, Labastie P, L'Hermite J-M, Poncharal Ph (1997) Phys Rev Lett 79:633
55. Durand G, Spiegelmann F (2001) Eur Phys J D 13:237
56. Vajda S, Lupulescu C, Merli A, Budzyn F, Wöste L, Hartmann M, Pittner J, Bonačić-Koutecký V (2002) Phys Rev Lett 89:213404
57. Heitz MC, Durand G, Spiegelman F, Meier C (2003) J Chem Phys 118:1282
58. Durand G, Heitz MC, Spiegelman F, Meier C, Mitrić R, Bonačić-Koutecký V (2004) J Chem Phys 121:9898
59. Heitz MC, Durand G, Spiegelman F, Meier C, Mitrić R, Bonačić-Koutecký V, Pittner J (2004) J Chem Phys 121:9906
60. L'Hermite J-M, Blanchet V, Le Padellec A, Lamory B, Labastie P (2004) Eur Phys J D 28:361
61. Guiang CS, Wyatt RE (2000) J Chem Phys 112:3580
62. Lakhlifi A, Chabbi H, Dahoo PR, Teffo JL (2000) Eur Phys J D 12:435
63. Naumkin FY, Wales DJ (2000) Mol Phys 98:219
64. Bihary Z, Gerber RB, Apkarian VA (2001) J Chem Phys 115:2695
65. Crepin C, de Pujo O, Bouvier B, Brenner V, Millié P (2001) Chem Phys 272:243
66. Naumkin FY, Wales DJ (2002) Comp Phys Comm 145:141
67. Balling LC, Wright JJ (1983) J Chem Phys 79:2941 ibid 81:675
68. Roncero O, Beswick JA, Halberstadt N, Soep B (1990) NATO ASI, Series B, 227:471
69. Boatz JA, Fajardo ME (1994) J Chem Phys 101:3472
70. Collier MA, McCaffrey JG (2003) J Chem Phys 119:11888
71. Tutein AB, Mayne HR (1998) J Chem Phys 108:308
72. Ben El Hadj Rhouma M, Berriche H, Ben Lakhdar Z, Spiegelman F (2004) Int J Quant Chem 99:495
73. Ben El Hadj Rhouma M, Spiegelman F, Ben Lakhdar Z (2006) Recent Advances of the Theory of Chemical and Physical Systems. In: Julien J-P, Maruani J, Mayou D, Wilson S, Delgado-Barrio G (eds.) Progress in Theoretical Chemistry and Physics, vol XV. Springer Berlin Germany p. 450
74. Tsoo C, Estrin DA, Singer SJ (1990) J Chem Phys 93:7187
75. Gross M, Spiegelmann F (1998) J Chem Phys 108:4148
76. Gross M, Spiegelmann F (1998) Eur Phys J D 4:219
77. Duplàa P, Spiegelmann F (1996) J Chem Phys 105:1492
78. Duplàa P, Spiegelmann F (1996) J Chem Phys 105:1500
79. Jonin C, Laporte P, Spiegelmann F (2002) J Chem Phys 117:3049, ibid 117:3059
80. Durand G, Duplàa P, Spiegelmann F (1997) Z Phys D Atoms Molecules and Clusters 40:177
81. Kutzelnigg W, Theor. Chim. Acta **68**, 445 (1985)
82. Kutzelnigg W, Klopper W (1991) J Chem Phys 94:1985
83. Bouvier B, Thesis, Université de Paris-Sud
84. Staib A, Borgis D (1995) J Chem Phys 103:2642