Electronic and structural properties of rare gas cation clusters

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ELECTRONIC AND STRUCTURAL PROPERTIES OF RARE GAS CATION CLUSTERS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemistry

by

Jose Alejandro Gascon
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to Fabiana
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We study structure and ground and excited state properties of rare gas cation clusters, $\text{Rg}_N^+$, for $N = 3 - 60$. The main goal is to understand how the positive charge is delocalized over the cluster and the relationship between cluster geometry and delocalization. $\text{He}_N^+$, $\text{Ar}_N^+$, and $\text{Xe}_N^+$ are selected as representatives of the rare gas elements. We perform Monte Carlo simulations to obtain finite temperature properties of the energy spectrum. The Hamiltonian of the system is based on a semiempirical model whose parameters are obtained through the fitting of experimental and calculated properties such as bond length and dissociation energy of small clusters ($N \leq 5$). Since rare gas cation clusters are formed by closed shell atoms with one electron deficiency, the Hamiltonian is constructed within a hole (electron deficiency) formalism, resulting in a single particle model. In addition, our model can treat polarization and dispersion energies as a many-body interaction which is very important for small clusters. We compare our results with experiments through calculations of photoabsorption cross section and magic numbers.
Clusters of atoms and molecules are the bridge between the gas phase and the solid state. In the early 1970s, the advent of new experimental tools such as lasers and modern flow reactors led to a considerable improvement in mass spectrometers as these are an essential tool in the study of clusters. This area of research was soon to become a field of its own, cluster science [1, 2]. From the beginning, rare gas neutral clusters were the subject of much research. For their simplicity, it seemed natural to consider these closed shell atom clusters as the benchmark for the development of experimental methods and theoretical concepts [3, 4]. Of particular interest was the study of stability and structure of such aggregates. Soon it was discovered the existence of magic numbers [5, 6, 7], these are particular numbers of atoms that conform clusters with exceptional stability. The first experiment was performed by Echt and co-workers [5] on Xe clusters, and was followed by experiments on Ar, and Kr clusters by Ding and Hesslich [6], and Stephens and King [7] on He clusters. In contrast to the magic numbers found in nuclei, which are a consequence of a shell effect in momentum space, in atomic rare-gas clusters they are purely geometric; this is, they result from a competition between
the repulsive atom core-atom core interactions and the tendency to maximize the number of nearest neighbor interactions. It was concluded that rare gas clusters form icosahedral structures [8] with high stability for clusters with closed geometric shells occurring at 13, 19, 55, 147, 548, etc. Since clusters in these experiments were often produced by ionization of neutral clusters followed by mass selection, experimentalists realized that the "neutral" cluster mass spectra were mainly due to the ions formed prior to mass selection and not to the distribution of neutral clusters [9, 10, 11, 12, 13]. Clear evidence of this observation is that Ar, Kr, and Xe [5, 6, 7] showed magic numbers at $N = 25$ which is a predicted magic number for the single charged clusters of Ar and Xe [12, 14, 15, 16]. This was the starting point for both experimental [17, 9, 11, 12, 13] and theoretical [18, 19, 20, 21, 22, 23, 24] interest in the rare gas cluster ions themselves. In addition, there was early interest in the study of rare gas cation dimers and trimers for their possible influence in the efficiency of excimers lasers that used rare gas-halide molecules [25, 26]. Ab initio calculations of the electronic structure of the dimers done for this purpose would latter become the basis for theoretical models of larger clusters such as the Diatomic-in-Molecules (DIM) method [27, 28, 29, 30]. In the last decade there has been sustained interest in the structure and dynamics of rare gas cation clusters, $\text{Rg}_N^+$, not only to investigate their electronic and structural properties but also because they serve as models for charge transfer, ion solvation, fragmentation dynamics, and for their use in understanding ionization processes [31]. In addition, theoretical models of $\text{Rg}_N^+$ can be extrapolated to the study of metal cation clusters, in particular to second row alkali metals such as magnesium [32, 33, 34, 35], which can yield new insights in the study
Figure 1.1: Diagrams of the HOMO’s for the rare gas trimers constructed with the valence $p$ atomic orbitals. Dashed lines indicate nodes, and dark lobes indicate negative amplitude. From the nodal structure it is clear that the $\Sigma_u^+$ state is more repulsive than the doubly degenerate $E'$ states, and therefore it is easier to remove one electron from $\Sigma_u^+$.

of insulator-metal transitions.

All rare gas cation trimers are linear and symmetrical, in contrast to the equilateral triangle geometry of their neutral counterpart. This can be explained in terms of the molecular orbital diagrams in Figure 1.1. This figure shows the HOMO’s for the two possible geometries of $\text{Rg}_3$ constructed from valence $p$ atomic orbitals. The same argument can be applied for $\text{He}_3$, using valence $s$ atomic orbitals. It follows from the nodal structure that the $\Sigma_u^+$ HOMO of the linear geometry is more repulsive than any of the doubly degenerate HOMO’s having symmetry $E'$. Therefore, the bonding on the linear structure becomes stronger after removing one electron relative to removing one electron from the triangular structure so that $\text{Rg}_3^+$ is linear. In addition, the $\text{Rg}_3^+$ triangular structure must exhibit a Jahn-Teller distortion, since the HOMO for this structure is doubly degenerate (this is also valid for $\text{He}_3^+$), though not likely to distort the geometry into a linear configuration. The central atom in
Figure 1.2: Hückel model of a linear chain of $N$ sites. $t$ is the hopping integral between two adjacent atomic orbitals. As $N$ increases the ground state tends toward the asymptotic value $E_0 - 2t$, where $E_0$ is the site energy.

$Rg_3^+$ carries about 50% of the charge and the two outer atoms carry 25% each. As a consequence of the delocalization on a third center, the equilibrium bond length of $Rg_3^+$ is larger than that of $Rg_2^+$. This is because the hole is in an anti-bonding state (see Appendix D): the more localized the hole is within two atoms the stronger is the attraction between them. Thus, since the central atom and one of the outer atoms in $Rg_3^+$ carry 75% of the charge their separation is larger than in $Rg_2^+$ where both atoms carry 100%. For this same reason the equilibrium bond length of $Rg_2$ is larger than that of $Rg_2^+$. All rare gas cation tetramers have basically two possible structures as the lowest in energy. One consists of a linear trimer as in $Rg_3^+$ with one neutral atom off to one side. This geometry is usually referred as T-shaped. The other one consists of a linear tetramer ion where the two central atoms carry about 84% of the charge and the two outer atoms carry 8% each. For all $Rg_4^+$, these two structures are basically isoenergetic, differing by less than 0.01 ev [23, 36, 37]. Whether one of these structures is the lowest energy geometry of $Rg_4^+$ depends on the competition between polarization energies and charge delocalization. The first one tends to concentrate neutral atoms around the ion core without a preferred direction and the second tends to place atoms
in the direction of delocalization. Adding extra atoms co-linearly does not, however, add stabilization indefinitely [24]. This can be understood considering a simple Hückel model of a linear chain of \( N \) sites (Figure 1.2). The eigenvalues are given by

\[
E_i = E_0 - 2t \cos \frac{i\pi}{N+1}, \quad i = 1, N
\]

where \( E_0 \) is the site energy and \( t \) is the hopping integral between two adjacent atomic orbitals. Assuming \( t > 0 \), the ground state is \( E_0 - 2t \cos \frac{1}{N+1} \) which tends to the asymptotic value \( E_0 - 2t \) as \( N \) increases. Although linear structures for \( N > 4 \) can be stable, none of the rare gas cation clusters has a linear geometry as the global minimum. Thus, for \( N > 4 \), atoms are concentrated in off-axis positions, either surrounding a linear trimer core or a linear tetramer core.

The main focus of this thesis is to understand structure and stability of \( \text{Rg}_N^+ \) clusters and the features of delocalization and their relationship to structure. As a point of reference for the comparison with experimental results, we have made particular emphasis in the calculation of photoabsorption cross section and magic numbers. The study of the evolution of absorption spectrum with cluster size gives us important insights about the interplay between delocalization and structure. We begin in Chapter 1 with a detailed description of the model used in our investigations. In the subsequent Chapters, we present results for \( \text{Ar}_N^+, \text{Xe}_N^+, \) and \( \text{He}_N^+ \), following the order in which they were studied during the course of our investigations of \( \text{Rg}_N^+ \). As He, Ar, and Xe span the rare gas column, we have not considered Ne, Kr, and Rn cation clusters. Studies that have focused exclusively on Ne and Kr clusters
can be found in the following references: [38, 39, 40, 36, 41, 42]. To our knowledge, there are neither experimental nor theoretical works on Rn clusters. We conclude in Chapter 5 remarking the main results of our work and compare our model with current approaches based on DIM. In Appendix A, we solve the problem for the eigenstates of Xe\(_2^+\) as it presents many important features of the theoretical description, spin-orbit interaction and many-body polarization. In Appendix B we described in detail the inclusion of spin-orbit interaction in the model Hamiltonian. In Appendix C we derive the explicit form of the Drude Hamiltonian, which contains the many-body polarization, for Rg\(_2\) and Rg\(_2^+\) and solve for its eigenvalues. Finally, in Appendix D we show molecular orbitals diagrams within a minimal basis set for Rg\(_2^+\) and Rg\(_3^+\) describing the correspondence between electronic wavefunctions and hole wavefunctions.
CHAPTER 2

THEORETICAL MODEL OF $Rg_N^+$

Here we consider a general model for the $p$-shell rare gases with many-body polarization (MBP) and spin-orbit coupling. In the next chapter we consider a 2-body model to study large Ar$_N^+$ clusters. In Chapter 5 we treat separately the model for helium, as the $s$ character of the basis functions involved leads to different functional forms and different dimension of the Hamiltonian. Our Hamiltonian uses six basis functions for each atom since the charge can be in a $p$-type orbital with spin up or down. The Hamiltonian has the following form:

$$H = H_{Rg-Rg} + H_{Rg^+Rg^-} + H_{MBP} + t + H_{SO}.$$  \hfill (2.1)

$H_{Rg-Rg}$ is the short range repulsion interaction between neutral Rg atoms and is given by

$$H_{Rg-Rg} = \sum_{k,\nu,\alpha} |k, \nu, \alpha\rangle \left[ \sum_{i,j\neq k} A e^{-BR_{ij}} \right] \langle k, \nu, \alpha |$$  \hfill (2.2)

where $|k, \nu, \alpha\rangle$ represents a $p$-type orbital on atom $k$ with orientation $\nu$ ($\nu = \hat{x}, \hat{y}, \hat{z}$) and spin $\alpha$ ($\alpha = \uparrow, \downarrow$), $i$ and $j$ label atoms, and $R_{ij}$ is the distance between atom $i$ and $j$. $H_{Rg^+Rg^-}$ is
the short range repulsion between the atom with the charge and the neutral atoms:

\[
H_{Rg^+ - Rg} = \sum_{k,\nu,\alpha} |k, \nu, \alpha\rangle \left[ \sum_{i \neq k} A^+ e^{-B^+ R_i} \right] \langle k, \nu, \alpha |.
\] (2.3)

\[H_{MBP}\] is the polarization energy of a system of \(N\) atoms in the presence of a charge:

\[
H_{MBP} = \sum_{k,\nu,\eta,\alpha} |k, \nu, \alpha\rangle D(k)_{\nu\eta} \langle k, \eta, \alpha |,
\] (2.4)

where the explicit form for \(D(k)_{\nu\eta}\), assuming a Drude oscillator model of fluctuating dipoles on each atom, is

\[
D(k)_{\nu\eta} = \sum_{i=1}^{3N} \frac{1}{2} \left[ \sqrt{\lambda_i(k)} - \frac{\langle \nu | X_i^2(k) | \eta \rangle}{\lambda_i(k)} - \omega_i \right].
\] (2.5)

where \(X_i(k)\) is the shift in the normal mode minimum due to the field from the charge on atom \(k\). Note that the energy associated with this term contributes to both diagonal and off-diagonal on-site elements. \(\lambda_i\) is the normal mode frequency in the absence of electric field and \(\omega_i\) is the unperturbed atomic Drude frequency. Equation 2.5 is derived in detail in the next section.

The form of the hopping term \(t\) is estimated from its form for a dimer: \(\langle \Psi_i | (V_i + V_j)/2 | \Psi_j \rangle\), where \(\Psi_i\) and \(\Psi_j\) are the wave functions of the charge being localized in atoms \(i\) and \(j\), respectively, and \(V_i\) is the potential energy of the charge interacting with atom \(i\). Assuming Slater 2\(p\)-type orbitals we obtain the off-diagonal matrix connecting atom \(i\) and \(j\):
\[ t_{ij} = I_t + \frac{R_{ij \pi}}{R_{ij}^2} (t_\sigma - t_\pi), \]  

(2.6)

where \( I_\nu \eta = \delta_\nu \eta \), \((R_{ij \pi})^\nu \eta = R_{ij \pi}^\nu R_{ij}^\eta \), and

\[ t_\pi = -ae^{-bR_{ij}}(1 + bR_{ij} + \frac{1}{3}b^2 R_{ij}^2), \]  

(2.7)

\[ t_\sigma = -ae^{-bR_{ij}}(1 + bR_{ij} - \frac{1}{3}b^3 R_{ij}^3). \]  

(2.8)

The hopping matrix between atom \( i \) and \( j \) is obtained by the direct product \( t = t_{ij} \otimes I_2 \), where \( I_2 \) is the spin-dependent \( 2 \times 2 \) identity matrix. It is interesting to notice that independent of the form of \( t_\pi \) and \( t_\sigma \), Eq. 2.6 is the general expression of the hopping matrix between \( p \)-type orbitals. In particular, it satisfies rotational invariance. One can take advantage of this by realizing that an atom produces a perturbation on the second atom so that the \( \sigma \) and \( \pi \) hopping terms are not strictly a result of the overlap of identical \( p \) orbitals. One can therefore use a form for \( t_\pi \) and \( t_\sigma \) that has different \( a \) and \( b \) values in Eqs. 2.7 and 2.8 (i.e: \( a_\pi, b_\pi, a_\sigma, \) and \( b_\sigma \)).

For the inclusion of spin-orbit interaction we have followed the semiempirical atoms-in-molecule (AIM) scheme proposed by Cohen and Schneider [43] in which the on-site off-diagonal elements only account for the spin-orbit coupling. In appendix C we derive in detail the spin-orbit Hamiltonian:

\[
H_{SO} = 2\delta \sum_k \sum_{\eta, \alpha, \nu, \beta} |k, \nu, \alpha\rangle \langle k, \nu, \alpha| L_k \cdot S_k |k, \eta, \beta\rangle \langle k, \eta, \beta|
\]  

(2.9)
where \( \delta \) is the spin-orbit coupling constant. For instance, for a 5-\( p \) orbital of Xe, \( \delta = -0.0160476 \) (a.u) \[44\]. The matrix elements \( \langle k, \nu, \alpha | \mathbf{L}_k \cdot \mathbf{S}_k | k, \eta, \beta \rangle \) are obtained by first evaluating the matrix elements \( \langle k, m_l, \alpha | \mathbf{L}_k \cdot \mathbf{S}_k | k, m_l', \beta \rangle \), where \( m_l (l \equiv 1) \) represents the spherical harmonic basis set. Then the matrix is transformed by a change of basis from \( |k, m_l, \alpha\rangle \) to \( |k, \nu, \alpha\rangle \equiv |k, \nu, \alpha\rangle \). Finally, the on-site matrix accounting for the spin-orbit coupling is

\[
H_{SO} = \begin{pmatrix}
0 & 0 & i\delta & 0 & 0 & \delta \\
0 & 0 & 0 & -i\delta & -\delta & 0 \\
-i\delta & 0 & 0 & 0 & 0 & i\delta \\
0 & i\delta & 0 & 0 & i\delta & 0 \\
0 & -\delta & 0 & -i\delta & 0 & 0 \\
\delta & 0 & -i\delta & 0 & 0 & 0
\end{pmatrix}
\] (2.10)

where \( i = \sqrt{-1} \).

### 2.1 Many-Body Polarization

We now present in detail the theory of many-body polarization (MBP). We follow the work by Cao and Berne \[45\] and treat the polarizability of the atoms using a Drude model. Since the diagonal matrix elements correspond to the charge being localized on one atom, we can write the Hamiltonian for the Drude oscillators as

\[
H = \sum_{i=1}^{N} \left[ \frac{\mu_i^2}{2\omega_i^2} + \frac{\mu_i^2}{2\alpha_i} \right] - \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \mu_i \cdot T_{ij} \cdot \mu_j - \sum_{i=1}^{N} \mu_i \cdot \mathbf{E}_i(k),
\] (2.11)
where the charge is localized on atom $k$, $\mu_i$ is the dipole moment of atom $i$, $T_{ij}$ is the dipole-dipole tensor whose matrix elements are given by

$$T_{ij}^{\nu\eta} = \frac{3R_{ij}^\nu R_{ij}^\eta - \delta_{ij}^{\nu\eta} R_{ij}^2}{R_{ij}^5} \times \gamma_n(R_{ij}, \sigma), \quad (2.12)$$

$\alpha_i$ is the polarizability of atom $i$, $\omega_i$ is the frequency of oscillator $i$, and $E_i(k)$ is the electric field at atom $i$ due to a charge on atom $k$, which for the moment is assumed a point charge.

We adopt a general idea proposed by Last and George [46], where the dipole-dipole tensor in Eq. 2.12 is scaled by the damping term $\gamma(R_{ij}, n)$ accounting for the overlap between two atoms. We propose here the form

$$\gamma_n(R_{ij}, \sigma) = \left[ 1 + \left( \frac{\sigma}{R_{ij}} \right)^{12} \right]^{(-1/n)}, \quad (2.13)$$

with $n = 4$.

Making the substitution $\mu_i = \sqrt{\alpha_i} \omega_i z_i$, in Eq. 2.11 the Hamiltonian becomes

$$\sum_{i=1}^{N} \frac{\dot{z}_i^2}{2} + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} z_i \cdot M_{ij} \cdot z_j - \sum_{i=1}^{N} \sum_{i \neq k} \sqrt{\alpha_i} \omega_i z_i \cdot E_i(k), \quad (2.14)$$

where the matrix $M_{ij}$ is defined as

$$M_{ij}^{\nu\eta} \equiv \omega_i^2 \delta_{ij}^{\nu\eta} - \sqrt{\alpha_i \alpha_j} \omega_i \omega_j T_{ij}^{\nu\eta} (1 - \delta_{ij}). \quad (2.15)$$
Let us define

\[ Z = (z_1, ..., z_k, ..., z_N), \]

\[ Q = (q_1, ..., q_k, ..., q_N), \]

\[ Y = (\sqrt{\alpha_1 \omega_1}E_1(k), ..., 0, ..., \sqrt{\alpha_N \omega_N}E_N(k)), \] (2.16)

where the 0 in the last definition is in the \( k \)th place. If \( M \) is diagonalized via \( Z = U \cdot Q \), where \( U \) is a unitary transformation, the Hamiltonian becomes

\[ H = \frac{1}{2} \dot{Q}^2 + \frac{1}{2} Q \cdot M' \cdot Q - Y \cdot U \cdot Q \] (2.17)

where \( M' \) is a diagonal matrix whose elements are the eigenvalues of \( M \). Defining

\[ X = Y \cdot U, \] (2.18)

then the Hamiltonian becomes

\[ H = \frac{1}{2} \sum_{i=1}^{3N} \dot{Q}_i^2 + \sum_{i=1}^{3N} \lambda_i \left( Q_i - \frac{X_i}{\lambda_i} \right)^2 - \frac{X_i^2}{\lambda_i} \] (2.19)

where \( \lambda_i \) are the eigenvalues of \( M \). This is the Hamiltonian of \( 3N \) independent harmonic oscillators with a ground state energy

\[ \sum_{i=1}^{3N} \frac{1}{2} \left( \sqrt{\lambda_i} - \frac{X_i^2}{\lambda_i} \right). \]
To finally obtain the interaction energy we need to subtract the energy of $3N$ independent Drude oscillators. The final MBP energy is obtained as

$$D = \sum_{i=1}^{N} \frac{1}{2} \left( \sqrt{\lambda_i} - \frac{X_i^2}{\lambda_i} - \omega_i \right). \tag{2.20}$$

We have assumed so far an electric field originated from a point charge. A more rigorous treatment assumes an anisotropic charge distribution corresponding to the orbital containing the charge. This higher order approximation seems to be crucial for Xe. If it is not included there is a tendency to produce non-directional forces which result in structures like those of the neutral species. For instance, for $\text{Xe}_4^+$ the lowest energy geometry would be a pyramid.

In the spirit of the Born-Oppenheimer approximation we assume that the time scale for motion of the charge is much longer than that of the Drude oscillators. Therefore, we must evaluate the matrix elements of the ground state energy of the Drude Hamiltonian, this is, $D^{\nu\eta} \equiv \langle \nu | D | \eta \rangle$. The only term that depends on orientation is $X_i^2(k)$. Its matrix element is calculated as follows:

$$\langle \nu | X_i^2 | \eta \rangle = \sum_\zeta \langle \nu | X_i | \zeta \rangle \langle \zeta | X_i | \eta \rangle,$$

where the sum is over the 3 $p$ orbitals on the charged atom. It is clear that the evaluation of $X_i^{\nu\eta}$ requires the evaluation of $\langle \nu | E_q(p) | \eta \rangle$, where $E_q(p)$ is the electric field on atom $q$ produced by the charge on atom $p$. Therefore we must evaluate the term

$$E_q(p)^{\nu\eta} = -\nabla_{R_{qp}} \phi(R_{qp})^{\nu\eta}, \tag{2.21}$$
which first requires
\[
\phi(R)^{\nu\eta} = \int d\mathbf{r} \psi_{\nu}(\mathbf{r}) \psi_{\eta}(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{R}|},
\]  
(2.22)

We assume \(\psi_{\nu}\) is a 2-\(p\) orbital, \(\psi_{\nu}(\mathbf{r}) = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha r^2}\) and \(c\) is a fitting parameter. The last integral can be evaluated for \(R >> \frac{1}{c}\):
\[
\phi(R)^{\nu\eta} = \left( \frac{1}{R} - \frac{3}{2c^2 R^3} \right) \delta^{\nu\eta} + \frac{9}{2c^2 R^5} \mathbf{R}^\nu \mathbf{R}^\eta.
\]  
(2.23)

Taking the gradient in Eq. 2.23 we obtain,
\[
\mathbf{E}^{\nu\eta} = \left( \frac{\mathbf{R}}{R^3} - \frac{9\mathbf{R}}{2c^2 R^5} \right) \delta^{\nu\eta} + \frac{45\mathbf{R}}{2c^2 R^7} \mathbf{R}^\nu \mathbf{R}^\eta - \frac{9}{2c^2 R^5} (\mathbf{e}_{\nu} \mathbf{R}^\eta + \mathbf{e}_{\eta} \mathbf{R}^\nu),
\]  
(2.24)

where \(\mathbf{e}_\nu\) is the unit vector in the \(\nu\) direction. The first two terms in Eq. 2.24 already contain the expected effect of a charge distribution acting parallel and perpendicular to the interatomic axis. That is, it has the same form as Eq. 2.6, a \(\sigma\) part and a \(\pi\) part. For computational simplicity, we only consider these two terms. We noticed that considering the extra term had a very small effect in the final results in the simulations. Finally, we also include a damping term on the contribution to the polarization energy coming from the electric field; \(E^{\nu\eta}(R)\) is scaled by \(\gamma_\alpha(R, \sigma^+)\).

### 2.2 Photoabsorption Spectrum

The procedure for calculating the photoabsorption spectrum is as follows: if \(|a\rangle = \sum c_{\nu\alpha} |i\nu\alpha\rangle\) is the eigenvector of the \(a\)th state, then the transition dipole between state 0 and \(a\) for a
A given configuration is given by
\[ \mu_{0a}^\xi = \langle 0 | r^\xi | a \rangle = \sum_{i,\nu,\alpha} (c_{0i\nu\alpha})^* c_{a\nu\alpha} R_i^\xi, \] (2.25)

where \( R_i^\xi \) is the position vector of atom \( i \), and \( \xi = x, y, \) or \( z \). For Eq. 2.25 we have adopted the simplified form used by Doltsinis et al [47]. Finally, the photoabsorption cross section is reported as a function of the wavelength:
\[ I(\lambda) = s_0 \hbar \lambda^2 \frac{1}{\Delta \lambda N_c} \sum_l \sum_a \frac{1}{\lambda_{0a}} |\mu_{0a}(l)|^2 \Theta(\lambda_{0a} - \lambda + \frac{\Delta \lambda}{2}) \Theta(\lambda + \frac{\Delta \lambda}{2} - \lambda_{0a}), \] (2.26)

where \( \Delta \lambda \) is the bandwidth in wavelength units, \( \Theta \) is the Heaviside step function, \( N_c \) the number of sampled configurations labeled by \( l \), and
\[ s_0 = \frac{1}{4\pi \varepsilon_0} \frac{4\pi^2}{3\hbar^2}. \]

The value of \( s_0 \) is, in atomic units, 0.095961 a.u.

### 2.3 Fitting Process

An important part in the construction of the Hamiltonian is the process of fitting the model parameters. This can be done by either using \textit{ab initio} calculations and experimental measures of structural and electronic properties, in general, of \( \text{Rg}_N^+ \) for \( N = 1 - 3 \) or both. In any case, the quality of the model depends on the overall quality of both the \textit{ab initio} cal-
culations and experiments. The fitting procedure is based on a least squares minimization. Let us consider a number of $M$ properties $x^i_0$, $i = 1, M$ that must be fit. For a given set of parameters $p$ the model leads to $x^i_p$ for these properties. An appropriate way to define a cost function, which will be minimized using a simulated annealing procedure [48], is

$$f_p = \frac{1}{M} \sum_{i=1}^{M} \left( \frac{x^i_p - x^i_0}{x^i_0} \right)^2.$$  

With this definition we can obtain an upper value for $f_p$ that produces an overall desired fit. For instance, if we require an maximum average error of 1% for each property, then

$$|\frac{x^i_p - x^i_0}{x^i_0}| < 0.01,$$

for all properties. Therefore,

$$f_p < 0.0001.$$

In general, in all our models we obtained costs functions in the range (0.0001, 0.001) which means a maximum average error in the range (2%, 3.2%).

### 2.4 Diatomics-in-Molecules (DIM)

The most common theoretical model of $\text{Rg}_N^+$ has been Diatomics-in-Molecules (DIM). It was first proposed by Ellison [49] and then applied by Kuntz and Valldorff [23] to $\text{Ar}_N^+$ and $\text{Xe}_N^+$. 

16
In the DIM a pair-wise interatomic potential is assumed and is derived from the ground and excited state curves of $\text{Rg}_2$ and $\text{Rg}_2^+$ in the following way: given the curves $^2\Sigma_u^+$, $^2\Pi_g$, $^2\Pi_u$, and $^2\Sigma_g^+$ of $\text{Rg}_2^+$ (assuming no spin-orbit interaction), obtained from *ab initio* calculations, the interatomic potentials $V_\sigma$, $V_\pi$, and hopping terms $t_\sigma$, $t_\pi$ are constructed knowing that

\begin{align}
E(^2\Sigma_u^+) &= V_\sigma - t_\sigma \\
E(^2\Pi_g) &= V_\pi + t_\pi \\
E(^2\Pi_u) &= V_\pi - t_\pi \\
E(^2\Sigma_g^+) &= V_\sigma - t_\sigma.
\end{align}

These four equations determine $V_\sigma$, $V_\pi$, $t_\sigma$ and $t_\pi$. In addition, the neutral-neutral interatomic potential $U$ is simply obtained from the ground state curve $^1\Sigma_g^+$, $U = E(^1\Sigma_g^+)$. Thus the on-site matrix of the Hamiltonian is constructed as

\begin{equation}
H_{ii} = \sum_{j=1, j \neq i}^{N} \left[ 2IV_\pi(R_{ij}) + \frac{R_{ij}R_{ij}}{R_{ij}^2}(V_\sigma(R_{ij}) - V_\pi(R_{ij})) \right] + \sum_{j,k \neq i}^{N} \frac{IU(R_{jk})}{k > j},
\end{equation}

where $R_{ij}$ is the distance vector between atom $i$ and $j$ and $I$ is the $3 \times 3$ identity matrix.

Finally, the off-site matrix connecting atom $i$ and $j$ is constructed as

\begin{equation}
H_{ij} = \left[ 2It_\pi(R_{ij}) + \frac{R_{ij}R_{ij}}{R_{ij}^2}(t_\sigma(R_{ij}) - t_\pi(R_{ij})) \right].
\end{equation}
Three body potentials arising from the interaction of induced dipoles can be easily included [24] as well as spin-orbit interactions [24, 50]. In the final chapter we will compare DIM with the model used in our work.

2.5 End Notes

CHAPTER 3

$\text{Ar}_N^+$ CLUSTERS

The electronic and geometric structures of argon cation clusters have received both experimental [51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 12, 6] and theoretical [61, 14, 62, 46, 63, 64, 65, 66, 67, 68, 15, 69] interest over the past few years. The focus has been to understand the extent of delocalization of the positive charge (hole) and the evolution of the photoabsorption cross section as a function of cluster size. Previous theoretical studies using a tight-binding model [67] and a diatomics-within-molecules (DIM) approach [61, 14] have predicted a relatively large blue shift in the photoabsorption spectrum between 3 and 7 atoms which is not seen in experiment. Neither model included many-body polarization (MBP), which may be important for polarizable atoms such as argon. Recent DIM calculations have included polarization effects through a 3-body interaction in the simulation of photoabsorption spectra. Grigorov and Spiegelmann [68] report calculation for $N = 3, 4, 8, 13$ and 19 at finite temperature while Doltsinis and Knowles [15] report simulations at 0 K for $N = 3$. However, there has yet to be a study that includes polarization for all clusters from $N = 3 - 23$. In this chapter, we use a semi-empirical tight-binding Hamiltonian that includes many-body
polarization to study $\text{Ar}^+_N$ clusters at finite temperature. We also calculate the photoabsorption spectra without using MBP for $N = 3 - 27$ and determine the minimum energy geometries at 0 K using MBP to investigate the most stable clusters in the range $N = 3$ to $N = 26$. Finally, using the 2-body model, this is without many-body polarization, we treat larger clusters from $N = 30$ to $N = 60$.

3.1 Model Parameters

For argon, we do not consider spin-orbit coupling. In terms of the model described in the previous chapter, this is done by setting the spin-orbit coupling to zero, and therefore reducing in half the dimension of the matrix Hamiltonian. In addition, we found a better fit by including extra terms in the functional form of the hopping terms. It is derived from the form of $\langle \Psi_i | T + V_i + V_j | \Psi_j \rangle$, where $\Psi_i$ and $\Psi_j$ are the wave functions of the hole being localized on atoms $i$ and $j$, respectively, $T$ is the kinetic energy, and $V_i$ is the potential energy of the hole interacting with atom $i$. Assuming Slater 2$p$-type orbitals we obtain, as in Eq. 2.6

$$t_{ij} = I(t_\pi + s_\pi) + \frac{R_{ij} R_{ij}}{R_{ij}^2} [(t_\sigma + s_\sigma) - (t_\pi + s_\pi)], \quad (3.1)$$

where

$$s_\pi = -a'e^{-bR_{ij}}(1 + bR_{ij} + \frac{2}{5}b^2 R_{ij}^2 + \frac{1}{15}b^3 R_{ij}^3), \quad (3.2)$$

$$s_\sigma = -a'e^{-bR_{ij}}(1 + bR_{ij} + \frac{1}{5}b^2 R_{ij}^2 - \frac{2}{15}b^3 R_{ij}^3 - \frac{1}{15}b^4 R_{ij}^4). \quad (3.3)$$
The parameters of the model are determined from known experimental values or by fitting the Ar\(_N\) and Ar\(_{N}^+\) ground and excited state properties for \(N = 1 - 3\). This is distinct from the work by Morales et al [67], in which only monomer and dimer properties were used to determine parameters. The polarizability and C\(_6\) coefficient for Ar are taken from the literature [70, 71]. To determine \(\omega_{Ar}\) and \(\omega_{Ar^+}\), we use the relation given by Cao and Berne [45] for a Drude oscillator model of the atoms, viz. \(C_6 = \frac{3}{4}\omega\alpha^2\) for a pure system and \(C'_6 = \frac{3}{4}\frac{\omega_1\omega_2}{\omega_1+\omega_2}\alpha_1\alpha_2\) for a mixture, where the \(\alpha\)'s are polarizabilities and the \(\omega\)'s are frequencies of the Drude oscillators. These two last equations are derived in Appendix D as a particular limit in the Drude model. \(\omega_{Ar}\) is determined with the knowledge of \(C_6\) and \(\alpha_{Ar}\). We consider Ar\(_2^+\) as a mixture of Ar and Ar\(^+\) and thus we need the frequency and polarizability of Ar. We obtain \(\alpha_{Ar^+}\) by using previously performed \textit{ab initio} calculations of the polarizabilities of Ar and Ar\(^+\) and scaling the experimental value of \(\alpha_{Ar}\) by the ratio of the polarizabilities determined in the \textit{ab initio} calculations. We assume that the ratio of \(\omega\)'s is the same as the ratio of ionization potentials of Ar and Ar\(^+\), which was then used to estimate \(\omega_{Ar^+}\) from \(\omega_{Ar}\). These two quantities were actually used later as fitting parameters. In summary, \(A, B, A^+, B^+, a, b, a', \sigma, \sigma^+, \omega,\) and \(\omega^+\) were determined by fitting to the bond length, dissociation and excitation energies for Ar\(_N\) and Ar\(_N^+\) with \(N = 2 - 3\). The model Hamiltonian for the case without MBP is described in the work by Morales et al [67] except for the modification on the hopping term that was described above. The parameters for the current models are shown in Table II.
Table 3.1: Parameters of the model Hamiltonian with and without MBP. All parameters, except $\alpha$ and $\alpha^+$ are used as fitting constants.

<table>
<thead>
<tr>
<th></th>
<th>with MBP</th>
<th>without MBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>80.845</td>
<td>172.520</td>
</tr>
<tr>
<td>$B$</td>
<td>1.8361</td>
<td>1.8314</td>
</tr>
<tr>
<td>$A^+$</td>
<td>1514.41</td>
<td>2164.39</td>
</tr>
<tr>
<td>$B^+$</td>
<td>2.1936</td>
<td>2.2823</td>
</tr>
<tr>
<td>$a$</td>
<td>1.5949</td>
<td>1.9159</td>
</tr>
<tr>
<td>$b$</td>
<td>1.9579</td>
<td>1.9782</td>
</tr>
<tr>
<td>$a'$</td>
<td>0.6495</td>
<td>0.6172</td>
</tr>
<tr>
<td>$\alpha$</td>
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<td>11.09</td>
</tr>
<tr>
<td>$\alpha^+$</td>
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<td></td>
</tr>
<tr>
<td>$\omega$</td>
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<td></td>
</tr>
<tr>
<td>$\omega^+$</td>
<td>2.2045</td>
<td></td>
</tr>
<tr>
<td>$C_6$</td>
<td></td>
<td>95.310</td>
</tr>
<tr>
<td>$C_6^+$</td>
<td></td>
<td>107.448</td>
</tr>
<tr>
<td>$\sigma$</td>
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<td>5.4341</td>
</tr>
<tr>
<td>$\sigma^+$</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Results

All calculations are performed at a temperature of 80 K. The initial configuration is obtained by combining a simulated annealing with a conjugate gradient minimization [72] for the model without MBP. The starting geometry for this procedure is generated by randomly placing the $N$th atom around the cluster of $N - 1$ atoms. The minimized geometry is then used as the initial configuration in the finite temperature calculations for both models, with and without MBP. A Monte Carlo simulation of 120,000 steps for small clusters (3-13) and 80,000 (14-23) for large clusters is performed to calculate the average properties.
Figure 3.1: Calculated photoabsorption cross section. The curves are vertically shifted $0.3\times10^{-16}\text{cm}^2$ from each other. a) From $N = 3$ to $N = 14$. b) From $N = 15$ to $N = 21$.

### 3.2.1 Photoabsorption Spectrum

In Fig. 3.1 we show the photoabsorption spectra as a function of the cluster size. Between $N = 3$ and $N = 14$ (Fig. 3.1.a) we observe three peaks in the spectra. The first peak is located at about 260 nm. It was seen experimentally by Johnson et. al [58]. This is commonly referred as a dimer remnant, although the average charge for the ground state is distributed in a trimer core for $N > 3$ [67]. In terms of atomic orbitals, such energies
correspond to states with no nodes between the central atom and its two neighbors \( (2^2\Sigma_u^+) \) [28]. A second peak is located at about 425 nm and is characterized by the symmetry \( 2^2\Pi_u \).

Although these transitions \( (1^2\Sigma_u^+ \rightarrow 2^2\Sigma_u^+, 2^2\Pi_u) \) are forbidden for a linear symmetric trimer, they emerge due to instantaneous vibrational symmetry breaking. A third and main peak is located at about 520 nm and is associated with the \( \text{Ar}_3^+ \) transition \( 1^2\Sigma_u^+ \rightarrow 1^2\Sigma_u^+ \). At \( N = 10 \) this main peak red shifts to a final location around 570 nm for \( N = 23 \). From \( N = 15 \) (Fig. 3.1.b) a high energy shoulder emerges and finally resolves at \( N = 21 \). This same trend occurs for the model without MBP for \( N > 14 \). However, without MBP, for \( N \leq 14 \) the spectra continue blue shifting and abruptly red shift at \( N = 14 \). For comparison with previous experimental and theoretical works, we calculate the wavelength \( (\lambda_{\text{max}}) \) at the maximum of the photoabsorption spectrum with a resolution \( \Delta \lambda = 5 \) nm. The results are shown in Figure 3.2., along with results without using MBP and experiment. A particular feature of the experimental spectra is the absence of blue shift for small clusters. Levinger et. al [60] (open triangles in Fig. 3.2) report spectra of \( \text{Ar}_N^+ \) for sizes \( N = 3 \) and \( N = 23 \). They claim that clusters between \( N = 4 \) and \( N = 15 \) present a similar spectrum to that of \( \text{Ar}_3^+ \) with a peak near 520 nm. Our spectrum for \( \text{Ar}_3^+ \) presents its peak at 525 nm and it is narrower than the spectrum obtained by Levinger et. al by about 30%. Consequently, the peak is higher by about 35%. We are not including spin-orbit coupling and zero-point energy effects which could lead to better agreement in terms of the width and height of the peak. Haberland et. al [59] (open circles in Fig. 3.2) report no blue shift from \( N = 3 \) to \( N = 6 \) after which they see mainly a red shift and finally a constant value for \( N > 20 \). Our
results using MBP agree very well with this trend. We find a maximum blue shift of 5 nm from $N = 3$ to $N = 7$ which is smaller than the error bars presented in the experiment by Haberland et al. From $N = 7$ there is virtually no blue shift. It is important to mention that our calculations are based on fitting the excitation energy for $\text{Ar}_3^+$ to 520 nm, therefore our spectra is expected to agree better with the spectra obtained by Levinger et al, especially for small clusters. In summary, the evolution of the maximum peak as a function of the cluster size agrees very well with both experimental works. Although the qualitative results
of the MBP model are similar to those without MBP for \( N > 14 \), it is clear that the inclusion of MBP is important for smaller clusters.

### 3.2.2 Hole Delocalization Using MBP

After each ten Monte Carlo configurations the atoms are labeled in order of decreasing charge in the ground state. These configurations are saved for the calculation of the average charge for the different regions of the spectrum using the square of the transition dipole as a weighting factor. For all clusters, the average charge distribution in the ground state is localized in a trimer core. Figs. 3 and 4 show the average charge in the excited states for different regions of the spectrum as a function of the \( n \)th atom (\( 1 \leq n \leq N \)). Fig. 3.3.a and 3.3.b show the excited state charge distribution for the UV region around 260 nm and the region around 425 nm for \( N = 4, 14 \) and 20. All cluster sizes follow the same trend, i.e: the hole is still localized in a trimer core. This is expected, since these two regions are already present in the photoabsorption spectrum for \( \text{Ar}_3^+ \). Fig. 3.3.c shows the excited state charge distribution for the main peak around 520 nm for \( N \leq 14 \). A common feature for these cluster sizes is the almost zero charge on the first atom (central atom). As \( N \) increases, the hole is smoothly delocalized over the solvating atoms (atoms labeled 4 to \( N \)) accompanying a decrease in charge on the core. This delocalization effect is correlated with the decreasing of the oscillator strength at the maximum of the peak and a consequent broadening of the photoabsorption spectrum. In our analysis of the main peak, we find contributions from three types of excited states. Two contributions are obvious for \( N > 14 \) and lead to the low and high energy peaks that become resolved by \( N = 21 \). A third contribution to the
main peak comes from a large number of excited states with small transition moments; we refer to these states as the background. To analyze the low and high energy regions of the main peak for \( N > 14 \) we only use those excited states whose values of the transition dipole are larger than certain cutoff. We choose the cutoff such that states with \( |\mu_{0a}(l)|^2 < 0.5 \)

Figure 3.3: Average hole distribution of the excited states as a function of the \( n \)th atom \( (n \leq N) \) for different regions of the spectrum. Atoms are labeled according to decreasing charge in the ground state. Representative cluster sizes are displayed. a) UV region. b) Region around 425 nm. c) main peak region around 520 nm for some cluster sizes with \( N < 15 \).
(a.u.)² are classified as the background. The cutoff value is chosen to resolve the low and high energy peaks and therefore to estimate the wavelength interval for each region. The intervals are (470 nm, 515 nm) for the high energy peak and (515 nm, 650 nm) for the low energy peak. Fig. 3.4.a and 3.4.b show the average charge for the high/low energy regions respectively. In the high energy region, about 60% of the charge is localized in the first 5
atoms, consistent with a higher kinetic energy for that relatively high localization. In the low energy region, the charge is a little more delocalized (50% over the first 5 atoms), consistent with a lower kinetic energy. For the background, the charge is completely delocalized over the entire cluster (Fig 3.4.c). Since the trimer core and the next two solvating atoms are the carriers of at least 50% of the charge, we investigate the average location of atoms 4 and 5 relative to the ion core and the average nodal structure of the electronic states. For the analysis of atom 4, each saved configuration is translated and rotated so that atom 1 is at the origin and atom 2 is on the positive $\hat{x}$ axis. The cluster is then rotated about the $\hat{x}$ axis so that atom 4 lies in the $\hat{x} \hat{y}$ plane with its $\hat{y}$ coordinate greater than zero. Two types of configurations arise, one with atom 4 near atom 2 (70% of the configurations) and the other with atom 4 near atom 3. A similar analysis was applied to the location of atom 5. We do not attempt to determine the correlations between the locations of atoms 4 and 5. Fig. 3.5.a shows the average geometry of the trimer core and the 4th solvating atom in its most probable position for the cluster with $N = 19$. This is a representative cluster size where low and high energy regions are distinguished from the main peak. Two geometries are shown corresponding to the high and low energy regions. The average orientation of the charge-carrying orbital on each atom is calculated by averaging the contributions from the three $p$ orbitals on each atom and is indicated in the figure. In the low energy region, atom 1 has almost no charge and the orbital on atom 4 overlaps constructively with the orbital on atom 2. In the high energy region atom 1 has about 13% of the charge and the orbital on atom 4 overlaps destructively with the orbital on atom 2 consistent with a higher energy.
Figure 3.5: Average geometry of the trimer core for $N = 19$ with: (a) the 4th solvating atom, and (b) the 5th solvating atom. The average nodal structure is also shown.

Fig 3.5.b shows the average geometry for atom 5. In both the low and high energy regions the overlap between atom 5 and atom 2 seems to be constructive, although in the low energy region the overlap is more $\sigma$ bond while in the high energy region is more $\pi$ bond. In the high energy state, the orientation of atom 5 also appears to be correlated with the orientation of atom 1.

### 3.2.3 Energy Optimization and Magic Numbers Using MBP

We calculate the minimum energy geometry for the model with MBP by using the Powell minimization procedure [72] over the saved configurations during the MC run for $N < 23$. The inclusion of MBP requires an $N \times N$ diagonalization for each diagonal term of the Hamiltonian, thus using conjugate gradient minimization (which requires the calculation of the gradient) would be practically impossible. Even using the Powell method the time
needed to achieve the optimized geometry is considerable. Therefore, for \( N = 20 - 27 \) we

![Graph showing relative binding energy as a function of cluster size. (●) Relative binding energy as a function of cluster size. (○) First energy difference. (■) Second energy difference.](image)

Figure 3.6: (●) Relative binding energy as a function of cluster size. (○) First energy difference. (■) Second energy difference.

apply the Powell minimization to a single geometry which is obtained by conjugate gradient minimization over saved configurations using the model without MBP. This is justified as the optimized geometries with and without MBP are the same than those obtained [14, 15]
in DIM calculations for the range of sizes $N = 20 - 27$.

There is no precise agreement among experiments [73, 12, 6] or between experiments and calculations [14, 67, 15] in the assignment of magic numbers. In addition, there have been different ways to describe the stability of a cluster in literature. Doltsinis et. al [15] report $\Delta E_N = E_{N-1} - E_N$ and $\Delta_2 E = E_{N+1} + E_{N-1} - 2E_N$ as a function of cluster size while Ikegami et. al [14] report the relative binding energy $\Delta E_N/\Delta E_{N+1}$ as a measure of the cluster stability. Magic numbers are somewhat dependent on which definition is used. We find magic numbers at $N = 13, 17, 19, 23$ and $25$ using $\Delta_2 E$ and $\Delta E_N/\Delta E_{N+1}$ and at $N = 13, 17, 19, 22$ and $25$ using $\Delta E_N$ (Fig. 3.6). Doltsinis et. al find a similar ambiguity under these definitions at $N = 22$ and $23$, although they find a magic number at $N = 16$ rather than $17$. Interestingly, Iwata et. al [14] find magic numbers at $N = 13, 16, 19, 22$ and $25$ for all three definitions.

### 3.3 Larger Clusters

In this section, we extend our simulations to $N = 60$, in order to probe two important issues: in the ground state, does the charge remain localized on 3 atoms for these larger clusters and, in the excited states, does the delocalization of charge over the entire cluster continue as atoms are added to the cluster? We use our model without many-body polarization in these studies to minimize computational effort and because we found only small differences between the two models for larger cluster sizes.
3.4 Results

Here we used the version of the Hamiltonian without many-body polarization. We performed Monte Carlo calculations at 80 K, using the following procedure: the initial configuration was generated by using a genetic algorithm to find the lowest energy geometry of a neutral $N$-atom cluster subject to a Lennard-Jones potential. From this initial configuration, a Monte Carlo simulation of 20,000 steps was performed at a temperature of 80 K. At each step, the $3N \times 3N$ Hamiltonian was diagonalized to find the ground and excited states. We used the ground state geometry in the Monte Carlo sampling process and used the excited states to calculate the average photoabsorption spectra as described in Ref. [74] for cluster sizes in the range $N = 30 - 55$. Due to the large computational effort, we did not calculate the photoabsorption spectrum for $N = 60$; however, we still sampled 20,000 configurations using an approximation that will be describe below (see comments on Fig. 3.7). These configurations were used in the charge distribution analysis. We also attempted to calculate the lowest energy geometries for some clusters that were reported to be the most stable clusters in an experiment performed by Harris et al. [12]. They found magic numbers at $N = 32, 34, 43, 46, 49,$ and $55$ in the range $N = 30 - 60$. Global optimization of these medium size clusters presented a formidable task. However, at this point, it was already known that the charge is localized mainly in a trimer core. This suggested we consider an effective number of atoms on which the charge could have significant amplitude. Similar approximations have been proposed before [75, 12]. Within our model Hamiltonian this is equivalent to making the size of the matrix as small as $9 \times 9$ (the charge can be in any of
the 3-\(p\) orbitals on each of the three core atoms). Fig. 3.7 shows that such approximation is very reasonable. It displays, for \(N = 31\), the ground state energy as a function of the number of atoms allowed to have charge. Here, atoms are sorted in order of decreasing charge in the ground state. Therefore, in our search for the lowest energy structures, we made the approximation that the charge was localized on a 3-atom core. From the Monte Carlo sampling described above, we saved configurations every 200 steps. The 1000 saved configurations for each cluster size were then minimized using a conjugate gradient algorithm, subject to our approximation. 0 K indicates the energy was calculated using the lowest energy geometry found in our conjugate gradient minimizations, while 80 K indicates the energy was calculated as an average from the Monte Carlo sampling. In any case, it is clear that
Figure 3.8: Lowest energy geometries for some representative clusters. For each cluster a front and a side view is displayed. The radii of the atoms are reduced for clarity. The 3 atoms that carry the charge in the ground state are colored black, next 22 atoms that complete the first solvation shell are colored grey, and the atoms forming the second solvation shell are colored white.

confining the charge to be on the first three atoms gives a good approximation to the total energy. Therefore, we used this approximation in the conjugate gradient method to search for the global energy for the cluster sizes mentioned above. Some of these geometries are shown in Fig. 3.8. There is a noticeable cylindrical symmetry for these clusters, reflecting the cylindrical symmetry of the 3-atom charged core. A common structure for the clusters in this range is a 25-atom core formed by 5 atoms (the middle 3 of which are the 3-atom core) relatively in line and four rings of 5 atoms each in between two adjacent atoms. In fact this is the lowest energy geometry of the 25 atom cluster [15, 14]. Our results for the photoabsorption spectra are shown in Fig. 3.9, along with a comparison to the work of Haberland et al. [59]. The position of the maximum peak was obtained by fitting a gaussian
Figure 3.9: Experimental and computed photoabsorption maxima, as a function of cluster size. The experimental work is from Ref. [59] and the computed maxima were obtained with a gaussian fit to the peak.

As can be seen, there is good agreement between theory and experiment for the location of the maximum in the photoabsorption spectrum. However, according to our data, there is still a small red shift. As we will see later, this may be due to a small, but continued, delocalization of the positive charge over the cluster for those excited states that contribute to the main photoabsorption peak.

We now turn to the charge distribution in both the ground and excited states. The average is done using the 1000 saved configurations from the Monte Carlo sampling. In performing the average, the square of the transition dipole is used as a weighting factor.
Figure 3.10: Calculated and fit to $N = 50$ photoabsorption spectrum. The solid line is the result of a gaussian fit done to estimate the maximum wavelength.

Shown in Fig. 3.11 are our results for the charge distribution in the ground state as a function of the $i$th atom ($1 \leq i \leq N$). Here, atoms are enumerated in order of decreasing charge in the ground state. Two representative clusters of the whole range are displayed, $N = 30$ and $N = 55$. There appears to be no change in the 3-atom core seen in smaller clusters. The asymmetry seen between the second and third atom is due to our numbering scheme and reflects the instantaneous difference in the two bond lengths resulting from the asymmetric normal mode vibration. Fig. 3.12 shows the charge distribution for those excited states contributing to the main peak for $N = 35$, 50, 55, and 60. The figure at the bottom is an augmented view of the upper figure. It can be seen that the charge continues to delocalize over the entire cluster, even between $N = 50$ and $N = 55$. However, the results from $N = 60$
Figure 3.11: Charge distribution in the ground state, as a function of atom number. Atoms were numbered in decreasing order of charge.

are in very close agreement with $N = 55$, suggesting that the delocalization has ended at $N = 55$, corresponding to the completion of the second solvation shell. This may explain the small red shift in the photoabsorption peak we find between $N = 43$ and $N = 55$.

We further analyzed the charge distribution of the excited states by calculating both the radial distribution of the charge and the radial distribution of the atomic positions. This was done by locating atom 1 on the origin and atom 2 on the $z$-axis. Thus, all distances were measured relative to the $z$-axis. Our results are shown in Fig. 3.13 for selected clusters. The dark line on these figures corresponds to the radial distribution of the atomic positions while the light line corresponds to the radial charge distribution. The sharp peak at $\rho = 0$ a.u of the atomic positions distribution corresponds, by definition, to atoms 1 and 2. The small
peak at $\rho \approx 0.5$ a.u contains the contribution from two atoms, atoms that are almost aligned with the $z$-axis (one of which is most likely the third atom in the 3-atom core). The peak at $\rho \approx 6$ a.u corresponds to the first solvation shell. Integration of this peak indicates there are approximately 20 atoms in this shell. In particular, for $N = 34$ it contains 18 atoms; for $N = 55$, 21 atoms; and for $N = 60$, 23 atoms. Integration of the charge distribution indicates that roughly 90% of the charge is confined to these atoms, adding roughly to 25 atoms (core + first solvation shell). The third peak corresponds to the second solvent shell. It contains 11, 23, and 25 atoms for $N = 34$, 55, and 60, respectively. At 0 K, one would not expect to
find atoms outside the second shell for \( N \leq 55 \). However, at finite temperatures there will be some atoms in the third shell (which we defined to be around \( \rho \simeq 16 \text{ a.u.} \)). Integration of

![Graphs showing charge distribution for excited states and atomic distribution for different values of N.](image)

Figure 3.13: Charge distribution for the excited states (light line) and atomic distribution (dark line), as a function of the radial distance to the \( z \)-axis. \( z \)-axis is defined to contain atom one and two.

this peak contributes 1, 7, and 8 atoms for \( N = 34, 55, \) and 60, respectively. Thus, although there are some atoms in the third shell, it can be seen that there is practically no charge on those atoms. Therefore, we find that the excited state charge delocalizes over the core, first, and second solvent shell supporting the tendency of the shift of the maximum wavelength to reach its bulk value beyond \( N \simeq 55 \).
3.5 Conclusions

We presented a novel method in including many-body polarization interactions in the hamiltonian model for $\text{Ar}_N^+ \ (N = 3 - 23)$. Comparing with experimental photoabsorption spectra we found very good agreement and noticed that inclusion of MBP is important for small clusters. We distinguished three components in main peak of the spectra. In two of them, the low and high energy regions, the average charge for the excited states at 80 K is mainly localized on 5 atoms. These atoms are the trimer core and two solvating atoms. These are the carriers of greater than 50% of the total charge. In the third region, the background, the charge is completely delocalized over the entire cluster. We used the Powell method to calculate the optimized geometries at 0 K and found the most stable clusters to be at $N = 13, 17, 19, 23$ and 25. We have used a 2-body model to study larger argon cation clusters. We find good agreement between our results and the experimental work of Haberland [59] for the position of the photoabsorption peak. Analysis of the ground electronic state demonstrates that the charge is localized in a 3-atom core for all cluster sizes studied. The excited states that contribute to the photoabsorption peak demonstrate charge delocalization over many atoms, up to the second solvation shell. Our calculation for $N = 60$ indicates no further charge delocalization for the excited state when a third solvation shell is added. The geometries found for these clusters are of cylindrical symmetry, corresponding to the linear, 3-atom charged core in the ground state.

Our calculations suggest that the excited states correspond to charge delocalization of the first and second solvation shells. The cluster sizes studied here are about half the size of
the smallest stable doubly charged Ar clusters, where stable \( \text{Ar}^{2+}_N \) clusters occurs at around \( N = 90 \) \cite{76, 77, 78} or about twice the number of atoms need to “contain” the excited state charge in a singly charged cluster. As our model can be modified to treat doubly charged clusters, such a study will be the focus of future work.

### 3.6 End Notes

In this chapter we present experimental and computational studies of the photoabsorption spectrum of Xe\textsubscript{N}\textsuperscript{+} clusters for \textit{N} = 3 – 30. We focus mainly on a unique feature not seen in lighter rare gas cation clusters. In Xenon, there are two families of isomers whose ground states consist on neutral atoms surrounded either a linear trimer ion core or a linear tetramer core. Interconversion of these two isomers appears to be present at temperatures as low as 60 K. Recent theoretical studies [79, 61, 68, 50, 47, 67, 74, 80] have investigated the extent of charge delocalization by combining information obtained from photoabsorption experiments [58, 60, 56, 81, 82] and from theoretical calculations of the charge density. Experiments using photoabsorption and photodissociation methods have studied He [82, 83], Ar [58, 60, 56, 81], and Xe clusters [81, 84] which are good representatives of the rare gases. An understanding of the spectral features requires a detailed understanding of the evolution of both ground and excited states as a function of cluster size. The absorption spectrum of large clusters appears to evolve continuously from that of the trimer. For He\textsubscript{N}\textsuperscript{+} the maximum of the absorption line has a very small red shift of approximately 16 nm [82] from He\textsubscript{3}\textsuperscript{+} to He\textsubscript{30}\textsuperscript{+}. \textit{Ab initio}
and diatomics-in-molecules calculations [37, 85, 86] show He$_N^+$ has a linear trimer ion core as its lowest energy geometry for $N = 3 - 8$. The small shift of the absorption line seen in the experiment suggests that the linear trimer core remains basically unperturbed by the solvating atoms. On the other hand, Knowles and Murrel [86] found structures with a dimer ion core as the most stable geometries for $N = 9 - 16$. For Ar$_N^+$, the red shift is about 90 nm [81] for this same range of $N$. Simulations at 80 K suggest that the ground state of the cluster is a trimer core even for clusters as big as Ar$_{60}^+$ [80]. The shift of the absorption peaks results from a delocalization of charge density in the excited states over the solvating atoms [61, 67, 74, 14]. Simulations [61, 67, 74] also revealed a second peak splitting from the main peak at around Ar$_{15}^+$ and then shifting to higher energies. The excited states contributing to the higher energy peak differ little from those contributing to the low energy peak in terms of the relative amount of charge on the solvating atoms and the core atoms. The difference lies in different nodal structure [14, 67, 74]. For Xe, the red shift in the photoabsorption spectrum from Xe$_3^+$ to Xe$_{30}^+$ is 200 nm. The high energy peak is now clearly present and well resolved in the experimental absorption spectra of Xe$_N^+$. Early discussions of these results suggested that these features were due to a development to a tetramer core [81]. It was also suggested that two families of isomers could be coexisting, one with a linear trimer core and other with a linear tetramer core [81]. This hypothesis is quite plausible if we notice that the difference in energy between the T-shaped configuration for Xe$_4^+$ (trimer core) and its linear isomer (tetramer core) is only 100 K, according to Kuntz and Valldorf [23]. This difference is in the range of the estimated temperature in the experiment by Haberland et al. Such small
differences in energy were actually predicted for Ar$_4^+$. Kuntz and Valldorf found a difference of just 10 K, while very recent calculations by Hrivnak and Kalus [87] found a difference of 30 K. Recent experiments by Issendorff et al. [88] using photofragmentation show clear evidence of the coexistence of both isomers in Xe$_4^+$ and Ar$_4^+$. On the other hand, Doltsinis [50] has shown that a trimer core model can reproduce the experimental photoabsorption spectrum of Xe$_{13}^+$ in terms of positions of the peak maxima. It is important to mention here that in the experimental report by Haberland and co-workers [81], only the absorption line shapes of Xe$_3^+$ and Xe$_{19}^+$ were displayed. For the rest of the clusters in the range 3 to 30, only the evolution of the maximum peaks with cluster size was shown. By combining simulation and experiment we will show that many of the features of the line shape are consistent with the coexistence of two families of isomers.

4.1 Model Parameters

The parameters of the model are determined from known experimental values or by fitting the Xe$_N$ and Xe$_N^+$ ground and excited state properties for $N = 1 - 3$. As we will discuss in detail in the next section, we also fit the difference in energy between the trimer and tetramer core structures of Xe$_5^+$ to be less than 100 K. The parameters $A$, $B$, $A^+$, $B^+$, $a_\pi$, $a_\sigma$, $b_\pi$, $b_\sigma$, $c$, $\omega_{Xe^+}$, $\omega_{Xe^+}$, $\sigma$, and $\sigma^+$, described in Chapter 1, are determined by fitting the bond length, dissociation, and excitation energies for Xe$_N$ and Xe$_N^+$ with $N = 2 - 3$ to their corresponding experimental values. To determine initial values for $\omega_{Xe^+}$ and $\omega_{Xe}$, we use the relation given by Cao and Berne [45] for a Drude oscillator model of the atoms, viz. $C_6 = \frac{3}{4} \omega_\alpha^2$ for a
Table 4.1: Parameters of the model Hamiltonian. All numbers are in atomic units.

<table>
<thead>
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<th>Value</th>
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<tr>
<td>$B$</td>
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<tr>
<td>$A^+$</td>
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</tr>
<tr>
<td>$\sigma^+$</td>
<td>1.86120</td>
</tr>
</tbody>
</table>

pure system and $C_6' = \frac{3}{4} \frac{2\omega_1\omega_2}{4\omega_1+\omega_2} \alpha_1 \alpha_2$ for a mixture, where the $\alpha$’s are polarizabilities and the $\omega$’s are frequencies of the Drude oscillators. The polarizability and $C_6$ coefficient for Xe are taken from the literature [89, 90]. $\omega_{Xe}$ is determined with the knowledge of $C_6$ and $\alpha_{Xe}$. We consider Xe$^+_2$ as a mixture of Xe and Xe$^+$ and thus we need the frequency and polarizability of Xe$^+$. We obtain $\alpha_{Xe^+}$ by using \textit{ab initio} calculations of the polarizabilities of Xe and Xe$^+$ and then making $\alpha_{Xe^+}$ equal to the literature value of $\alpha_{Xe}$ times the ratio of the polarizabilities determined in the \textit{ab initio} calculations. We assume that the ratio of $\omega$’s is the same as the ratio of ionization potentials of Xe and Xe$^+$, which was then used to estimate initial values for $\omega_{Xe^+}$ from $\omega_{Xe}$. The parameters of the model are shown in Table 4.1.
4.2 Simulations

All calculations are performed at a temperature of 60 K. A Monte Carlo (MC) simulation of 200,000 steps for small clusters (3-9), 100,000 for medium size clusters (10-15), and 60,000 for larger clusters (16-26) is performed to calculate statistical averages. In all cases an initial equilibration of 2000 steps is performed at 80 K. The starting geometry of each cluster is obtained by scaling the interatomic distances of the known minimum energy geometries of \( \text{Ar}_N^+ \) so that the lowest distance corresponds to the known experimental values of the trimer bond length of \( \text{Xe}_3^+ \).

As discussed above, the main hypothesis to test is whether the photoabsorption spectra can reveal the existence of two family of isomers. Therefore, one should expect the difference in energy between the two isomers for a given cluster to be such that both configurations are sampled at the temperature estimated in the experiment (60 K-100 K). Although there is no quantitative agreement between the calculated binding energies of both types of isomers [23, 24, 46], all models have given a difference in energy small enough so that after adding entropy effects it is conceivable that both types of isomers are present under experimental conditions.

The isomers seen in the simulations contain either a linear trimer core or a linear tetramer core. For instance, for \( \text{Xe}_4^+ \) the tetramer core and trimer core isomers are shown in Figure 4.1 (darker shades represent more charge), they are referred as ”linear” and ”T-shaped”, or \( \text{Xe}_4^+ \) and \((\text{Xe}_3^+)\text{Xe}\) respectively. For \( \text{Xe}_5^+ \) the tetramer core and trimer core isomers are shown in Figure 4.2, these geometries are referred as \((\text{Xe}_4^+)\text{Xe}\) and \((\text{Xe}_3^+)\text{Xe}_2\) respectively.
In our model, in general, we use experimental data for \( Rg_2, Rg_2^+, Rg_3^+ \) to fit the parameters. Now, since Xe presents a set of isomers whose difference in energy appears to be crucial in interpreting the experiment, we also fit the difference in energy between \((Xe_4^+)Xe\) and \((Xe_3^+)Xe_2\) to different values less than 100 K. We found that a difference of 6 K \(((Xe_3^+)Xe_2\) being lower in energy) presented the best agreement with the experiment. We chose the \(Xe_5^+\) isomers rather than the \(Xe_4^+\) isomers for this fitting because there is no experimental spectrum available for \(Xe_4^+\). It is clear that this is a qualitative fitting, and that the detailed calculation of the energies goes beyond the scope of this work. The main idea is to perform a simulation in which both family of isomers are sampled and compare the resulting spectra with experimental spectra.
4.2.1 Sampling Technique

The existence of two isomers separated by a large energy barrier can lead to what is called "broken ergodicity" in the sampling process. In fact, we found that using a standard Monte Carlo (MC) technique the transition rate between the two isomers was very low. In order to generate transitions between the two isomers, we supplemented the standard Metropolis sampling with a method that attempts transitions from one isomer to another with appropriate trial transition probabilities so that detailed balance is satisfied. In our simulations, most moves are of the standard Metropolis MC type. Local moves are attempted with a probability $T(R \rightarrow R') = 1/\Delta$ within a local region, where $\Delta$ is the maximum step size in one direction. A second type of move is attempted with a probability $P_J$ (approximately 10%) designed to jump from the energy basin of one isomer to the energy basin of the other isomer. The trial transition probability from a configuration $\{R\}$ in the initial basin to a
configuration $\{R'\}$ in the second basin is defined as

$$T(\{R\} \rightarrow \{R'\}) = \frac{1}{2} \left[ e^{-C \sum_{j=1}^{N} (R'_j - R_j)^2} + e^{-C \sum_{j=1}^{N} (R'_j - R_f)^2} \right]. \quad (4.1)$$

$\{R^{i(f)}\}$ represents the set of $3N$ coordinates of the minimum energy configuration of the initial (final) basin, and $C$ is an adjustable constant. It is chosen to obtain an appropriate acceptance ratio for the non-local moves. The underlying assumption in Eq. 4.1 is that the attempted configuration $\{R'\}$ is selected in the vicinity of $\{R_f\}$ with a probability

$$e^{-C \sum_{j=1}^{N} (R'_j - R_f)^2},$$

which assumes a very simplified harmonic approximation on each basin. The acceptance probability is then defined as

$$A(\{R\} \rightarrow \{R'\}) = \min[1, q(\{R\} \rightarrow \{R'\})];$$

where

$$q(\{R\} \rightarrow \{R'\}) = \frac{T(\{R\} \rightarrow \{R'\}) \rho(\{R'\})}{T(\{R'\} \rightarrow \{R\}) \rho(\{R\})},$$

and $\rho(\{R\}) = \exp(-\beta U(\{R\}))$ is the Boltzmann probability. This method is similar to the scheme proposed by Rossky et al [91].

In $Xe_N^+$ there are, actually, many local minima that are relevant at the temperatures of interest ($< 100 \text{ K}$). However, they can be separated into two families that correspond to geometries where neutral atoms surround either a linear trimer core or a linear tetramer.
core. One member of each family is chosen for a given cluster size and used as the template in the trial transition probability for the non-local jumps. This does not prohibit the system from exploring other isomers within each family, as these isomers can be sampled simply by diffusion during standard Metropolis moves. Since transition among isomers within a family occurs relatively easy, any of these isomers can be used as templates. For some cluster sizes we obtained templates by using the T-shaped and linear geometries for Xe\textsuperscript{4+} as seeds, then constructing larger clusters by adding atoms surrounding either core and finally locally minimizing these configurations. For other cluster sizes, we generated the templates by performing a high temperature Monte Carlo sampling and then locally minimizing stored configurations.

4.3 Experimental Spectra

The experimental photoabsorption cross section for Xe\textsuperscript{4+} for most of the clusters in the range 3 to 30 are presented in Figures 4.3, 4.4, and 4.5 in the range (500 nm, 1000 nm). The experimental apparatus is described elsewhere [92]. In the range (200 nm, 500 nm) the cross section exhibits another peak. Experimental spectra of the this last region were reported in reference [81]. From these spectra we notice the following features: for Xe\textsubscript{3} there is only one peak in the region (500 nm, 1000 nm), at \( N = 5 \) splitting of the main peak begins, and two peaks are resolved for larger clusters into high and low energy peaks. The low energy peak has roughly twice the intensity as the high energy peak, a point that will be important later in the discussion.
Figure 4.3: The absolute photoabsorption cross section in Å² of hot $\text{Xe}_N^+$, $N = 3 - 10$ is plotted against the wavelength in nanometers. The error bars give the statistical error only.
Figure 4.4: As in Fig. 4.3, but for $N = 11 - 16$. 
Figure 4.5: As in Fig. 4.3, but for $N = 26 - 30$. For the two largest cluster sizes measured, the experimental error in the total photoabsorption cross section can be up to a factor of two too large.
4.4 Calculated Spectra

In Figures 4.6 and 4.7 we present the spectra for most of the clusters from $N = 3$ to $N = 26$ in the range (200 nm, 1200 nm). The agreement with the experiment in terms of position of all peaks and their relative heights is remarkable. The absolute heights of the calculated spectra are larger by an average factor of 2, and the widths are comparable, except for the smallest clusters. Since we are using a model with only a limited number of excited states, we should expect larger oscillator strengths for each transition, since the oscillator strengths must satisfy the Thomas-Reiche-Kuhn sum rule [93]. This will manifest itself in our spectrum with the larger peak heights seen in our results. Another possibility for differences is the potential of different experimental “effective” temperatures for different cluster sizes. In addition, we have not included zero point motion, which would tend to broaden our peaks. A quantitative comparison of calculated and experimental spectra is best done by comparing oscillator strengths. This is done for a few clusters in Fig. 4.8. Despite the expected larger calculated oscillator strengths, the trends are reasonably well reproduced. In light of the expected differences between the two sets of spectra, we deem the agreement between calculations and experiment to be very good. Figure 4.9 shows a general comparison of the maximum peaks as a function of cluster size including those peaks in the range (200 nm, 500 nm) whose experimental values were reported in reference [81]. From the experimental spectra, it can be observed that the maximum wavelength of the high energy peak reaches a value of 600 nm at $N = 9$ and it remains there. The high energy peak in the calculated spectra reaches that value more slowly and is not resolved until $N = 10$. 

55
Figure 4.6: Simulated photoabsorption spectrum for clusters in the range (3-11).
Figure 4.7: Simulated photoabsorption spectrum for clusters in the range (13-26).
Figure 4.8: Oscillator strength as a function of clusters size for 13, 15, 19, 26. Experiment corresponds to hollow squares, simulations correspond to solid squares.

In order to analyze the possible contributions of the two isomers to the photoabsorption spectra, we performed simulations on each basin separately, making sure that there was no interconversion between the two isomers. Figure 4.10.a shows the spectra for the two isomers of Xe$_5^+$, (Xe$_4^+$)Xe and (Xe$_3^+$)Xe$_2$. The (Xe$_3^+$)Xe$_2$ isomer presents a maximum peak around 675 nm, while (Xe$_4^+$)Xe has a maximum around 775 nm. These two values agree quite well with the experimental values of the high and low energy peaks centered at 667 nm and 761 nm respectively. The templates for each basin were presented in Figure 4.2. The thermodynamic average in Figure 4.10.b exhibits a line shape very similar to the experimental
line shape suggesting that the isomers coexist, and that the isomer with a tetramer core is more abundant. At this point, one might be tempted to assign the high energy peak to the trimer core and the low energy peak to the tetramer core. However, the same analysis on larger clusters shows that the isomer with a trimer core also develops a low energy peak whose intensity, as we will show below, becomes comparable to the intensity of the high energy peak at around $N = 13$. The isomer with a tetramer core, however, appears to contribute mainly but not entirely to the low energy peak. All these observations can be brought together in the analysis of $\text{Xe}_{13}^+$. Figure 4.11.a shows the spectra for the two

![Figure 4.9: Comparison between simulation and experiment of the energies of the photoabsorption maximum peaks as a function of cluster size.](image-url)
isomers of $\text{Xe}_{13}^+$. The isomer $(\text{Xe}_{3}^+)\text{Xe}_{10}$ correspond to the well known icosahedral structure. This is the obvious choice for a template with a trimer core. The template for the isomer

![Diagram](image.png)

Figure 4.10: a) Simulated photoabsorption spectrum for the isomers $(\text{Xe}_{4}^+)\text{Xe}$ (tetramer core), and $(\text{Xe}_{3}^+)\text{Xe}_2$ (trimer core). Squares on the tetramer core line shape are displayed to clearly distinguish both lines. b) Simulated photoabsorption spectrum for the thermodynamic average of both isomers. Temperature of the simulation is 60 K. Note that the profile of the line shape agrees very well with the experimental cross section of $\text{Xe}_{5}^+$. $(\text{Xe}_{4}^+)\text{Xe}_9$ is shown in Figure 4.12. Simulations using the sampling technique described in previous section show that both structures are very likely to be present at 60 K. In Figure
4.11.a, it is important to observe that the \((\text{Xe}^+)_9\text{Xe}_{10}\) presents both low and high energy peaks and that their maximum wavelength, 780 nm and 600 nm respectively, agree well with the experimental values of 805 nm and 580 nm respectively. This was already pointed out by Doltsinis [50] who therefore suggested that the existence of a tetramer core isomer

![Figure 4.11: a) Simulated photoabsorption spectrum for the isomers \((\text{Xe}^+)\text{Xe}_9\) (tetramer core), and \(\text{Xe}^+\text{Xe}_{10}\) (trimer core). Squares on the tetramer core line shape are displayed to clearly distinguish both lines. b) Simulated photoabsorption spectrum for the thermodynamic average of both isomers. Temperature of the simulation is 60 K. Note that the profile of the line shape agrees very well with the experimental cross section of \(\text{Xe}_{13}^+\).](image-url)
may not be necessary to describe the experimental results. However, the thermodynamic average (Figure 4.11.b), which includes both isomers, produces a line shape that matches the experimental line shape better not only in position of the peaks (810 nm, 600 nm) but also in their relative heights suggesting again that both families of isomer coexist at 60 K. Before analyzing larger clusters than Xe$_{13}^+$, it is important to emphasize the relationship between charge delocalization and geometry. Because of the directionality of the $p$-orbitals, rare gas cation clusters tend to form linear subunits defined by the two atoms with the largest amount of charge. Regardless the structure of the surrounding atoms, delocalization of the charge appears to depend strongly on the overlap of the $p$-orbitals in the direction defined by the linear subunit. With this in mind, it is clear whether a given structure will present a trimer, a tetramer or perhaps larger units of charge. By symmetry, the charge density in the ground state will be basically an even function about the center of mass of the linear core. That is, an even number of atoms on the linear core presents a tetramer

![Side view and front view of tetramer core isomer of Xe$_{13}^+$.](image)

Figure 4.12: Front (a) and side (b) views of the tetramer core isomer of Xe$_{13}^+$.

core while an odd number of atoms presents a trimer core, and the amount of charge on each
atom of the core depends on interatomic distances and dihedral angles in case the linear core is bent. For instance, the closed shell structures of $\text{Xe}_{13}^+$, $\text{Xe}_{19}^+$, and $\text{Xe}_{25}^+$ have a trimer, tetramer and trimer core, respectively. Although the geometry of $\text{Xe}_{31}^+$ with a linear core of 6 atoms may not be the one with the lowest energy, it will present a tetramer core. Therefore, any cluster in this range may have either of these two cores or, as in the case of smaller clusters than $\text{Xe}_{13}^+$, a bimodal distribution of charge if both types of isomers are present at finite temperature. In order to investigate this distribution and whether a trimer core and a tetramer core may coexist or alternate in the sequence of cluster sizes, we have defined a simple quantity, $\Delta q = q_1 - q_2 + q_3 - q_4$, where $q_1$, $q_2$, $q_3$ and $q_4$ are the charges of the four
Figure 4.14: Distribution of $\Delta q$ for clusters in the range (4-11). In all cases, a bimodal distribution can be observed, consequence of the co-existence of isomer with a trimer and tetramer core.
atoms with the largest amount of charge in decreasing order. Structures with a trimer a core have a $\Delta q$ close to 0.5 while for structures with a tetramer core it is close to 0. For instance, for $\text{Xe}_{11}^+$, $\Delta q = 0.5$ for $(\text{Xe}_{11}^+)\text{Xe}_8$ and $\Delta q = 0.003$ for $(\text{Xe}_{11}^+)\text{Xe}_7$. In Figure 4.13 we show the distribution of $\Delta q$, $P(\Delta q)$, at 60 K for the two isomers of $\text{Xe}_{11}^+$. Notice that the distribution of $\Delta q$ for the tetramer core isomer is much broader than the distribution for the trimer core. This is probably due to the asymmetric stretching mode that leads to an instantaneous trimer structure. On the other hand, the structure $(\text{Xe}_{11}^+)\text{Xe}$ cannot have a small distortion in which the resulting geometry resembles a linear tetramer. Therefore, for any cluster we can expect for $P(\Delta q)$ to exhibit a distribution similar to one of those
in Figure 4.13 or a combination of both. Figure 4.14 shows the distribution of $P(\Delta q)$ for some clusters in the range (4-13). In all figures, a bimodal distribution is apparent. This shows what the analysis of the photoabsorption spectra had already suggested, that is, the co-existence of isomers with a trimer and tetramer core with more or less similar abundance. Figure 4.15 shows the distribution of $P(\Delta q)$ for some clusters in the range (14-19). The distribution for $Xe_{14}^+$ shows that the most likely isomer is the one with a trimer core. On the other hand, for $Xe_{19}^+$, the most likely isomer is the one with a tetramer core. $Xe_{15}^+$ appears to mark the point of transition from trimer to tetramer core. For the clusters in the range
(20-25) the transition is now from a tetramer to a trimer core (Figure 4.16). Interestingly, the point of transition is $\text{Xe}^{+}_{21}$ whose structure is equivalent to that of $\text{Xe}^{+}_{15}$. That is, $\text{Xe}^{+}_{15}$ and $\text{Xe}^{+}_{21}$ both have two atoms in addition to the closed shell structures of $\text{Xe}^{+}_{13}$ and $\text{Xe}^{+}_{19}$ respectively.

4.5 Conclusions

We presented finite temperature simulations and experimental determination of the photoabsorption line shape in $\text{Xe}_N^+$ clusters for $N = 3 - 30$. The theoretical model considers polarization and dispersion energies as a many-body interaction. We found that two families of isomers co-exist at 60 K for $N \leq 13$, one with a linear trimer core and the other with a linear tetramer core. This has a clear manifestation on the photoabsorption spectrum which gives information of the relative abundance of these two families of isomers. It was particularly in this range of size where the transition between the basin of one isomer and the basin of the other isomer is very unlikely to occur using a standard Metropolis method. To obtain reliable thermodynamic averages, it was necessary to supplement the Metropolis sampling with a method that attempts non-local transitions from one isomer to another.

For $N = 14 - 19$, the structure of the charge core starts with a trimer for $\text{Xe}_{14}^+$ and ends with a tetramer for $\text{Xe}_{19}^+$, being $\text{Xe}_{15}^+$ the point of transition. For $N = 20 - 25$, the charged core exhibits a transition from a tetramer core to a trimer core, being $\text{Xe}_{21}^+$ the point of transition. It was pointed out that the structure of the charge distribution can be simply understood in terms of the number of atoms on the axis that contains the charge core.
CHAPTER 5

He$_N^+$ CLUSTERS

From a theoretical and computational perspective, the calculation of the electronic properties of He$_N^+$ presents the most simple problem of the rare gas cation clusters. However, early DIM calculations found a strong limitation in that even when the He$_2^+$ and He$_2$ energy curves used as inputs were extremely accurate, the predicted geometry of He$_3^+$ was not consistent with the geometry obtained by accurate ab initio calculations; while DIM predicted an asymmetric linear trimer [94, 95], ab initio calculations predicted a symmetric linear trimer [94, 37], consistent with the geometry of the other rare gases. Attempts to include 3-body terms through interaction of induced dipoles [94] found no significant improvement. However, Knowles et al [96, 86] included 3-body terms by directly extracting their contribution from accurate ab initio calculations of the He$_3^+$ potential energy surface (PES), and then generating analytical forms for the 3-body matrix elements. As expected, they found the correct geometry for He$_3^+$ (D$_{\infty h}$) and argued that 4-body terms are less important for treating larger clusters. It is at first unexpected that 3-body terms seem to be more important in helium clusters than for heavier rare gases. Knowles and Murrel [86] argued that this is probably due to the very
short equilibrium bond length of He$_2^+$ and He$_3^+$ which may lead to a strong overlap of the atomic orbitals.

We have shown in previous chapters that our model for Rg$^+_N$ can include many-body effects. Helium clusters present, therefore, a good opportunity to test the many-body polarization used in our model. In this chapter we will show that our model predicts the correct geometries for small clusters and that the magic numbers predicted for larger clusters agree remarkably well with experiments of mass spectroscopy. Finally, we will compare our results on excitation energies and cross section with experimental measures done by Haberland’s group [82]. We also considered a model based on 2-body interactions. This is, we used pair-wise additive potentials for the different interactions between multipoles: $\alpha/R^4$, $C_6/R^6$, $C_8/R^6$, and $C_{10}/R^6$. Although it does not predict the correct geometry for He$_3^+$, as expected, it helps to find structures with a dimer or a tetramer ion core as it will be explained below.

5.1 Model Hamiltonian

The Hamiltonian for helium clusters uses one $s$ basis function per atom and has the following form:

$$H = H_{\text{He-He}} + H_{\text{He}^+-\text{He}} + H_{\text{MBP}} + t.$$  \hspace{1cm} (5.1)

$H_{\text{He-He}}$ is the short range repulsion interaction between neutral He atoms,

$$H_{\text{He-He}} = \sum_k |k\rangle \left[ \sum_{i,j\neq k} U(R_{ij}) \right] \langle k|,$$  \hspace{1cm} (5.2)
where \( |k\rangle \) represents a \( s \) orbital on atom \( k \), \( i \) and \( j \) label atoms, \( R_{ij} \) is the distance between atom \( i \) and \( j \), and

\[
U(r) = A \exp(Br)(1 + C/r).
\] (5.3)

\( H_{\text{He}^+ - \text{He}} \) is the short range repulsion between the atom with the charge and the neutral atom:

\[
H_{\text{He}^+ - \text{He}} = \sum_k |k\rangle \left[ \sum_{i \neq k} U^+(R_{ki}) \right] \langle k|,
\] (5.4)

where

\[
U^+(r) = A^+ \exp(B^+r)(1 + C^+r + D^+r^2).
\] (5.5)

In equations 5.3 and 5.5 we have used different forms than those used for argon and xenon because they were necessary to obtain a good fit due to their extra flexibility. Forms like these were also used by Knowles and Murrel to fit \textit{ab initio} curves [86]. \( H_{\text{MBP}} \) accounts for the polarization and dispersion energy of a system of \( N \) atoms in the presence of a charge:

\[
H_{\text{MBP}} = \sum_k |k\rangle D(k) \langle k|,
\] (5.6)

where the explicit form for \( D(k) \), assuming a Drude oscillator model of fluctuating dipoles on each atom, is

\[
D(k) = \sum_{i=1}^{3N} \frac{1}{2} \left[ \sqrt{\lambda_i(k)} - \frac{X_i^2(k)}{\lambda_i(k)} - \omega_i \right].
\] (5.7)

\( X_i(k) \) is the shift in the normal mode minimum due to the field from the charge on atom \( k \). \( \lambda_i \) is the normal mode frequency in the absence of electric field, and \( \omega_i \) is the unperturbed
atomic Drude frequency. Equation 5.7 was basically derived in Chapter 2. In section 5.3 we will derive new terms that depend on the character of $s$ orbitals and discuss a different functional form for the damping functions introduced in Chapter 2.

The form of the hopping term $t$ is estimated from its form for a dimer: \( \langle \Psi_i | (V_i + V_j)/2 | \Psi_j \rangle \), where $\Psi_i$ and $\Psi_j$ are the wave functions of the charge being localized in atoms $i$ and $j$, respectively, and $V_i$ is the potential energy of the charge interacting with atom $i$. Assuming 1$s$-orbitals we obtain the off-diagonal term of the matrix Hamiltonian connecting atom $i$ and $j$:

\[
t_{ij} = ae^{-bR_{ij}}(1 + bR_{ij}).
\]

(5.8)

### 5.2 2-body Model

For the 2-body model the He-He potential is extracted completely from the semi-empirical potential of Aziz et al [97]. The Aziz potential has the following form:

\[
U(r) = \epsilon U^*(r)
\]

(5.9)

where

\[
U^*(r) = A^* \exp(-B_1 r + B_2 r^2) - F(r, \delta) \sum_{j=0}^{2} \frac{C_{2j+6}}{r^{2j+6}}
\]

(5.10)
Table 5.1: Parameters of the Aziz potential. All numbers are in atomic units. All figures are not significant, they are included to avoid round-off errors

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.65921668</td>
</tr>
<tr>
<td>B_1</td>
<td>1.91269769</td>
</tr>
<tr>
<td>B_2</td>
<td>-0.06009169</td>
</tr>
<tr>
<td>(\delta)</td>
<td>7.9334101</td>
</tr>
<tr>
<td>C_6</td>
<td>1.46115485</td>
</tr>
<tr>
<td>C_8</td>
<td>14.11206797</td>
</tr>
<tr>
<td>C_10</td>
<td>183.5343316</td>
</tr>
</tbody>
</table>

with

\[
F(r, \delta) = \exp\left[\frac{(\delta/r - 1)^2}{2}\right], \quad r \leq \delta
\]

\[
= 1, \quad r > \delta.
\]

The values of the parameters of this potential are listed on Table 5.1. The potential in Eq. 5.5 includes now attractive terms originated from dispersion and polarization:

\[
U^+(r) = A^+ \exp(B^+r)(1 + C^+r + D^+r^2) - F(r, \sigma^+)\left(C_6 \frac{r^6}{r^6} + \frac{\alpha}{2r^4}\right).
\]

For the hopping term we use a more general form than that in Eq. 5.8 which allows a better fitting. This is,

\[
t_{ij} = ae^{-bR_{ij}}(1 + b_1 R_{ij} + b_2 R_{ij}^2).
\]
5.3 Helium Features in the MBP Model

In Chapter 2 we saw that we needed to consider a distribution of charge rather than a point charge as producing the electric field. Following the same idea, we now obtain the electric field due to a s-type charge density. We must evaluate the term,

\[ E_q(p) = -\nabla_{R_{qp}} \phi(R_{qp}), \]  \hspace{1cm} (5.15)

where \( E_q(p) \) is the electric field on atom \( q \) produced by a distribution of charge on atom \( p \).

First, we must evaluate,

\[ \phi(R) = \int d\mathbf{r} \psi(\mathbf{r}) \psi(\mathbf{r}) \frac{1}{|\mathbf{r} - \mathbf{R}|}, \]  \hspace{1cm} (5.16)

where \( \psi \) is a 1s orbital, \( \psi(\mathbf{r}) = \sqrt{c^3/\pi} e^{-cr} \). \( c \) will be used as a fitting parameter. The last integral can be solved exactly:

\[ \phi(R) = \frac{1}{R} \left( 1 - e^{-2cR} \left( 1 + cR \right) \right) \]  \hspace{1cm} (5.17)

Taking the gradient in Eq 5.17 we obtain,

\[ E = \frac{R}{R^3} \left( 1 - e^{-2cR} \left( 1 + 2cR + 2c^2 R^2 \right) \right). \]  \hspace{1cm} (5.18)

Then, the vector \( \mathbf{Y} \) is evaluated using \( E \) as described on Eq. 2.16.

We discussed in Chapter 2 also the need to include damping terms to account for the
overlap between two atoms. In Helium the choice of the right damping function appears to be crucial. The reason is due to the very short equilibrium bond length of He$_2^+$ compared to that of He$_2$. In helium, the ratio of these two lengths is 0.36, while for argon and xenon is 0.66 and 0.72 respectively. We use here the same damping function used in the Aziz potential in Eq. 5.12. The dipole-dipole matrix $T_{ij}^{\nu\eta}$ in Eq 2.12 is then multiplied by $F(R_{ij}, \sigma)$. As described in Chapter 2, we also include a damping term for the electric field, this is, $E$ is multiplied by $F(R_{ij}, \sigma^+)$. 

5.3.1 Model Parameters

The parameters of the MBP model are determined by fitting ground and excited state properties of He$_2$, He$_2^+$, and He$_3^+$. Unlike the fitting process used in argon and xenon clusters, we fit the curves for the ground and excited states of He$_2^+$ to the ab initio curves calculated by Carrington et al [98]. For He$_2$, we fit the equilibrium bond length and dissociation energy to the experimental values $R_e = 3.0$ Å and $D_e = 0.0009$ ev [99]. Here it is important to mention that the most accurate semi-empirical potential of He$_2$ are those obtained by Aziz et al [97]. Since we include many-body interactions we cannot use this potential. However, Aziz et al use analytical terms that can be related to different types of interactions. Now, the many-body polarization that we use in our model accounts, in the case of Rg$_2$, for the dispersion energy (i.e terms like $C_6/r^6$). Therefore, one could, in principle, subtract the $C_6/r^6$ from Eq. 5.10 and use the rest of the terms as an effective attractive part. Then, only the parameters in the many-body Hamiltonian are used to fit the ground state properties of He$_2$. We tried this approach and found that it was not possible to fit simultaneously the
Table 5.2: Parameters of the model Hamiltonian with and without MBP. All parameters, except $\alpha$ and $\alpha^+$ are used as fitting constants. All numbers are in atomic units. All figures are not significant, they are included to avoid round-off errors.

<table>
<thead>
<tr>
<th></th>
<th>with MBP</th>
<th>without MBP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>0.6454535</td>
<td></td>
</tr>
<tr>
<td>$B$</td>
<td>2.1941467</td>
<td></td>
</tr>
<tr>
<td>$C$</td>
<td>19.395705</td>
<td></td>
</tr>
<tr>
<td>$A^+$</td>
<td>8.6930016</td>
<td>3.0225747</td>
</tr>
<tr>
<td>$B^+$</td>
<td>3.3433590</td>
<td>3.5817667</td>
</tr>
<tr>
<td>$C^+$</td>
<td>-1.5581000</td>
<td>-4.5376363</td>
</tr>
<tr>
<td>$D^+$</td>
<td>2.7591343</td>
<td>16.4620005</td>
</tr>
<tr>
<td>$a$</td>
<td>0.8541924</td>
<td>3.0225747</td>
</tr>
<tr>
<td>$b$</td>
<td>1.4383381</td>
<td>1.53041137</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.3827</td>
<td>1.3827</td>
</tr>
<tr>
<td>$\alpha^+$</td>
<td>0.271</td>
<td></td>
</tr>
<tr>
<td>$\omega$</td>
<td>1.4270923</td>
<td></td>
</tr>
<tr>
<td>$\omega^+$</td>
<td>3.4901147</td>
<td></td>
</tr>
<tr>
<td>$\sigma$</td>
<td>7.8562971</td>
<td></td>
</tr>
<tr>
<td>$\sigma^+$</td>
<td>5.4395353</td>
<td>6.92874395</td>
</tr>
<tr>
<td>$b_1$</td>
<td>-0.039367349</td>
<td></td>
</tr>
<tr>
<td>$b_2$</td>
<td>0.109939543</td>
<td></td>
</tr>
</tbody>
</table>

excited state properties of $\text{He}_2^+$ and $\text{He}_3^+$. Finally we fit the dissociation energy of the $D_{\infty h}$ geometry of $\text{He}_3^+$ to the *ab initio* calculations done by Rosi and Bauschlicher [37] (0.17 ev). As a result of this fitting process, our model predicts a symmetric linear trimer as the lowest energy minimum with a bond length of $R = 2.367 \, a_0$ which agrees very well with all current *ab initio* calculations [40] (2.34 $a_0$).

Is important to mention here that, although the fitting of the $D_{\infty h}$ dissociation energy of $\text{He}_3^+$ somehow forces our model to predict the right geometry of the trimer, this is possible because of the many-body structure of the model. At the same time it highlights a quality of this model over DIM, this is the ability to incorporate properties of larger clusters. Even
Table 5.3: \(R_e\) and \(D_e\) for the ground state of \(\text{He}_2\), \(\text{He}_2^+\), and \(\text{He}_3^+\) for the MBP (I) and 2-body (II) models. Other experimental and theoretical results are also listed. All numbers are in atomic units. All \(R_e\) and \(D_e\), except the experimental ones, do not include zero-point energy motion.

<table>
<thead>
<tr>
<th></th>
<th>(\text{He}_2)</th>
<th>(\text{He}_2^+)</th>
<th>(\text{He}_3^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_e)</td>
<td>5.556 this work I</td>
<td>2.094 this work I</td>
<td>2.367 this work I</td>
</tr>
<tr>
<td></td>
<td>5.612 this work II</td>
<td>2.061 this work II</td>
<td>2.087,3.734 this work II</td>
</tr>
<tr>
<td>(D_e)</td>
<td>3.4658 (\times 10^{-5}) this work I</td>
<td>0.090929 this work I</td>
<td>0.00653 this work I</td>
</tr>
<tr>
<td></td>
<td>3.4630 (\times 10^{-5}) this work II</td>
<td>-0.091582 this work II</td>
<td>0.001317 this work II</td>
</tr>
<tr>
<td></td>
<td>3.4630 (\times 10^{-5}) [97]</td>
<td>0.090892 [100]</td>
<td>0.00625 [37]</td>
</tr>
<tr>
<td></td>
<td>3.3075 (\times 10^{-5}) [99] (exp.)</td>
<td>0.090638 [98]</td>
<td>0.00717 [86]</td>
</tr>
</tbody>
</table>

without MBP, by fitting properties of larger clusters, the model incorporates many-body properties implicitly.

The parameters of the 2-body model are determined by fitting only the ground and excited curves of \(\text{He}_2^+\) calculated by Carrington et al [98]. The parameters of both models are listed on Table 5.2. All parameters, except \(\alpha\) and \(\alpha^+\) are used as fitting constants. \(\alpha\) is obtained from \textit{ab initio} calculations in reference [98]. We perform a calculation of \(\alpha^+\) using GAUSSIAN 98 with the basis set cc-pV5Z. From the values of \(\alpha\) and \(\alpha^+\), and \(C_6\) from the Aziz potential, we obtained initial values for \(\omega\) and \(\omega^+\) as described in section 3.1. Table 5.3 shows the predicted values of bond length and dissociation energy for \(\text{He}_2\), \(\text{He}_2^+\), and \(\text{He}_3^+\) that result from the fitting process described above for both models. Other \textit{ab initio} and experimental values are also listed. Notice that we use a least square minimization technique in fitting our values, and therefore the predicted values are slightly different than
the expected values. Figure 5.1 shows the predicted curves for the ground and excited states (solid line) of \( \text{He}_2^+ \) for both models and the curves calculated by Carrington et al [98] (solid squares).

## 5.4 Structure and Energies of \( \text{He}_N^+ \)

The first calculations on \( \text{He}_N^+ \) with \( N > 3 \) were performed by Rosi and Bauschlicher [37] for \( N = 2 - 7 \) at two different levels of theory, SCF (Self Consistent Field) and MCPF (Modified Coupled Pair Functional). Only at the MCPF level the correct geometry for \( \text{He}_3^+ \)
was obtained. At this level of theory, Rosi and Bauschlicher [37] found that the global minimum energy geometries of clusters with $N = 4 – 7$ consisted of a linear trimer core with neutral atoms weakly attached on equatorial positions. These structures are similar to those found in argon and xenon clusters except that in these last, neutral atoms are attached to the trimer core asymmetrically (i.e: between the central atom and one of its neighbors). For $\text{He}_4^+$ they also found linear geometries, having the charge in a dimer core, less than 0.31 kcal/mol (156 K) above the T-shaped global minimum. Interestingly, this appears to be a common feature of all cation rare gas tetramers. Similar results for this same range of clusters, were found by Staemmler [85], who presented the first calculations of excitation energy. Knowles and Murrel were the first to calculate structure and stability of larger clusters up to $N = 16$. They found that the global minimum structures have a trimer ion core for $N < 9$ and a dimer ion core for $N = 9 – 16$. According to this result, one could expect a significant change in the absorption spectrum as the structure of the cluster has a transition from a trimer to a dimer core. Photoabsorption experiments on $\text{He}_N^+$ done by Haberland’s group [82] have shown, however, that the absorption spectra of $\text{He}_3^+$, $\text{He}_4^+$, $\text{He}_{10}^+$, $\text{He}_{21}^+$, and $\text{He}_{30}^+$ remains basically unchanged throughout this range. The absorption line in $\text{He}_3^+$ is centered at 5.34 ev (-0.1/+0.2 ev). This value agrees with the value for the excitation energy of $\text{He}_3^+$ calculated by Staemmler (5.5 ev) [85] for which he found a linear symmetric trimer as the lowest energy geometry. Haberland et al [82] then suggested that $\text{He}_3^+$ remains the structural core of larger clusters. Therefore, our goal is to calculate excitation energies for clusters in the range 3-30 and study the possible dependency of the absorption line with the
Table 5.4: Atomization energies $E$ and dissociation energies $D_e$ of helium clusters

<table>
<thead>
<tr>
<th>$N$</th>
<th>$E$/ev</th>
<th>$D_e$/ev</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-2.6546</td>
<td>0.1777</td>
</tr>
<tr>
<td>4</td>
<td>-2.6900</td>
<td>0.0353</td>
</tr>
<tr>
<td>5</td>
<td>-2.7254</td>
<td>0.0355</td>
</tr>
<tr>
<td>6</td>
<td>-2.7602</td>
<td>0.0348</td>
</tr>
<tr>
<td>7</td>
<td>-2.7950</td>
<td>0.0348</td>
</tr>
<tr>
<td>8</td>
<td>-2.8258</td>
<td>0.0308</td>
</tr>
<tr>
<td>9</td>
<td>-2.8526</td>
<td>0.0268</td>
</tr>
<tr>
<td>10</td>
<td>-2.8852</td>
<td>0.0326</td>
</tr>
<tr>
<td>11</td>
<td>-2.9139</td>
<td>0.0287</td>
</tr>
<tr>
<td>12</td>
<td>-2.9322</td>
<td>0.0184</td>
</tr>
<tr>
<td>13</td>
<td>-2.9467</td>
<td>0.0145</td>
</tr>
<tr>
<td>14</td>
<td>-2.9674</td>
<td>0.0207</td>
</tr>
<tr>
<td>15</td>
<td>-2.9788</td>
<td>0.0114</td>
</tr>
<tr>
<td>16</td>
<td>-2.9822</td>
<td>0.0033</td>
</tr>
</tbody>
</table>

structure of the ion core. In order to obtain the global minimum geometries we performed a genetic algorithm minimization for clusters in the range 3-16 using the MBP model. The atomization and dissociation energies of these structures are listed in table 5.4. Figure 5.2 shows these energies as a function of cluster size along with \textit{ab initio} [37] and DIM-based [86] calculations. We found that clusters up to 13 have a trimer ion core, and for 14 to 16 they have a tetramer core, in disagreement with the calculations by Knowles and Murrel [86]. For instance, for He$^{+}_{14}$, by a tetramer core we mean a linear core of four atoms where the two central atoms carry about 80% of the charge and the two outer atoms about 10% of the charge. Figure 5.3.a shows the global minimum geometry of He$^{+}_{14}$. Notice that it has icosahedral symmetry. In contrast to the rest of the rare gases, it is formed by 14 atoms rather than 13 atoms. Figure 5.4 shows $-D_e/E \equiv (E_{N} - E_{N-1})/E_{N}$ as a function of cluster
size as a measure of stability. Results by Knowles and Murrel [86] are also shown. Our results indicate that, for $N = 3 - 16$, 10 and 14 are magic numbers while Knowles and Murrel found magic numbers at 5, 7 and 10 in this range. A more rigorous measure of stability is the quantity $\Delta_2 E \equiv E_{N-1} + E_{N+1} - 2E_N$. Under this definition, only 14 is a magic number in our model, nevertheless, a peak in $-D_e/E$ versus $N$ is a clear measure of stability.

Interestingly, mass spectroscopy experiments on He$_N^+$ ($N < 16$) done by Kobayashi et al [102] have revealed magic numbers at 10 and 14 in perfect agreement with our results. In addition to these numbers, experiments by Stephens and King [7] showed also 7 as a magic number. We are, therefore, confident that the icosahedral structure that we found for
He$_{14}^+$ is the most stable geometry. To our knowledge, this structure has not been identified before. We believe that this structure may be the lowest energy geometry in the model of Knowles and Murrel and that it may have been missed in their minimization procedure. Certainly, finding global minima is a difficult task. We also performed a genetic algorithm minimization for the 2-body model. In fact, for this model we found an icosahedral structure for He$_{14}^+$ which was then locally minimized using the MBP model after which it relaxed to the geometry shown in figure 5.3.a. Interestingly, the geometry of He$_{14}^+$ for the 2-body model has a dimer ion core, yet it also has an icosahedral structure (figure 5.3.b) where the two central atoms carry about 95% of the charge.

### 5.4.1 Photoabsorption Spectrum

All calculations are performed a 20 K using 20,000 iterations. The evolution of the absorption line with cluster size appears to be consistent with the other rare gases studied here. That is, as the size increases the main peak splits into a low and high energy peak with the
Figure 5.4: Cluster stability as a function of cluster size. In our model magic numbers are indicated by peaks at 10 and 14.

low energy peak being higher in intensity. However, the simulated absorption spectrum of helium clusters fails to reproduce the main features of the experiment [82]. The experimental spectrum of He$_3^+$ exhibits a peak of 0.22 Å$^2$ at 5.34 ev in agreement with early \textit{ab initio} calculations of 5.5 ev done by Staemmler [85]. Our spectrum for He$_3^+$ (see figure 5.5) has a maximum peak of 1.75 Å$^2$ at 4.25 ev. For He$_8^+$ however, a high energy peak appears at a position very similar to the experimental peaks. Figure 5.6 shows the evolution of the energy maxima with cluster size along with experimental data. The experimental spectra from $N = 3$ to $N = 30$ exhibits only one peak almost with a slight red shift in this range. It appears then, even though the energy surface of the dimer cation for both the ground and excited state are very accurate, the excitation spectrum of larger clusters does not compare
Figure 5.5: Photoabsorption cross section in $\AA^2$ for some clusters in the range $N = 3 - 30$ as a function of energy for the MBP model.
Figure 5.6: Evolution of maximum energy peak with cluster size. Our simulations using MBP are shown in solid squares. Our spectrum exhibits, starting at \( N = 8 \) two peaks. Experiments by Haberland et al [82] are also shown.

well with the experiment. Therefore, it remains uncertain and interesting to us why the experimental absorption line remains basically unchanged from \( N = 3 \) to \( N = 30 \), as if there were no solvation effects of the charge in the excited states, a feature that was revealed in argon and xenon, and that actually shows up in helium according to our calculations. Despite the good agreement with experiment in the determination of magic numbers, we can think a couple of reasons for why our model apparently fails. One reason has to do with the dipole approximation used in the MBP model. As we noticed before, the bond length of \( \text{He}_2^+ \) is very short compared with \( \text{He}_2 \). In Appendix C we show that the Drude oscillator model fails when \( R^3 < 2 \alpha \), this is, \( R < 1.4 \ a_0 \) which is close to the \( \text{He}_2^+ \) equilibrium bond
length of \( R < 2.042 \ a_0 \). Although the failure of the Drude model can be bypassed by the use of damping functions, the right selection of these functions it seems crucial in helium. Further study of this matter can improve the quality of our model. The second is related to the treatment of the helium nuclei as quantum particles. It is not surprising that of all rare gases, zero point energy effects are most important for helium. In fact, the width of the spectra is almost 10 times broader than the width of the simulated spectra, a clear evidence that zero-point energy must be taken into account. It might be possible then, that the high and low energy peaks are overshadow by this broadening effect. Quantum statistics can be introduced in our simulations, and it will be the subject of future studies.

5.5 Conclusions

We used a many-body polarization model and a genetic algorithm optimization to generate global minimum geometries for clusters from \( N = 3 \) to \( N = 16 \). The most stable clusters, characterized by the magic numbers 10 and 14, are in excellent agreement with experiments of mass spectroscopy [102, 7]. We found that the structure of \( \text{He}_2^+ \) has icosahedral symmetry with a tetramer ion core, although an icosahedral structure with a dimer ion core is also possible. The simulated photoabsorption spectrum presents similar features of those found in argon and xenon, this is a solvation effect that leads to a splitting of the main absorption peak at \( N = 8 \) that gradually changes as cluster size increases. However, these features are not found in the experimental photoabsorption spectrum performed by Haberland’s group [82]. We think that this might me caused by the difficulty of the Drude model to properly
described the necessary interactions at very small interatomic distances. The appropriate
description of damping effects should be taken into account to improve the model. It appears
that the inclusion of zero-point energy motion is also necessary to obtain a better agreement
of finite temperature excitation processes.
CHAPTER 6
CONCLUDING REMARKS

In studying rare gas cation clusters we have made particular emphasis in several aspects: 1) structure stability and magic numbers, 2) delocalization of the positive charge (hole), 3) relationship between structure and charge delocalization, and 4) manifestation of these effects on the photoabsorption cross section. We presented a novel method in including many-body polarization interactions in the model Hamiltonian. In the study of $\text{Ar}_N^+$ for $N = 3 - 60$ we noticed that the inclusion of many-body polarization was important for small clusters, this is $N \lesssim 13$, which coincides with the first complete shell of icosahedral symmetry. For argon, finite temperature Monte Carlo simulations showed that, in the ground state, the charge remains localized in a trimer core. Xe and He present also structures with a tetramer core. We pointed out that, since the delocalization of the charge in the ground state is strongly preferential to the direction of highest symmetry, this is one-dimensional, the number of atoms on this direction determine whether the charge spreads on an even or odd number of atoms on that direction. Because of surface effects, units of charge larger than a tetramer were not observed for the cluster sizes studied. Eventually, for much bigger clusters than
the ones studied, as the inner structure of the cluster becomes more periodic, larger units of charge could be expected as well as a more isotropic distribution of charge. Interesting questions arise from this about the delocalization of the charge near the phase transition, expected at much larger clusters, from an icosahedral lattice to a face-centered cubic in the case of $p$-valence rare gas clusters and hexagonal in the case of helium clusters.

As a general feature of the photoabsorption cross section, the main peak splits into a low and high energy peak as a result of the interaction between the excited states of the ion core (trimer or tetramer) and those of the solvating atoms. This effect is more pronounced in xenon since the spin-orbit interaction favors delocalization perpendicularly to the linear ion core as a result of the mixture of $p$ orbitals within an atom. For both Ar$_N^+$ and Xe$_N^+$, the simulated photoabsorption spectra agreed very well with the experimental spectra [56, 59, 81]. In Ar$_N^+$, we found that the excited states that contribute to the photoabsorption peak demonstrate charge delocalization over many atoms, up to the second solvation shell ($N \leq 55$). Calculations for $N = 60$ indicate no further charge delocalization for these excited state when a third solvation shell is added. In Xe$_n^+$, we found that at temperatures as low as 60 K, there can be two families of isomers, one with a linear trimer core and other with a linear tetramer core. With the combination of simulations and experiments we were able to demonstrate the existence of these families of isomers and their manifestation in the photoabsorption spectra. We found that, for $N \leq 13$, the transition between the basin of one isomer and the basin of the other isomer was very unlikely to occur using a standard Metropolis method. To obtain reliable thermodynamic averages, it was important
to supplement the Metropolis sampling with a method that attempts non-local transitions from one isomer to another.

We studied stability of He$_N$ clusters using many-body and 2-body polarization models, and a genetic algorithm optimization to generate global minimum geometries for clusters from $N = 3$ to $N = 16$. The resulting magic numbers were in excellent agreement with experimental magic numbers from mass spectroscopy [102, 7]. We found that the magic number 14 corresponds to a cluster with icosahedral symmetry which can have a dimer or a tetramer core. To our knowledge, such geometries have not been considered before in literature. Although the simulated photoabsorption spectrum exhibits similar features than those present in argon and helium clusters, this is the evolution of the absorption line shape resulting from solvation effects as cluster size increases, these features are not found in the experimental photoabsorption spectrum [82]. Zero-point energy motion is most likely the reason of such disagreement. In fact, the width of the spectra is almost 10 times broader than the width of the simulated spectra. Quantum statistics can be introduced in our simulations, and it will be the subject of future studies. We also pointed out that there is an intrinsic difficulty of the Drude model to properly describe interactions at very small interatomic distances occurring in helium clusters. To bypass this problem, the appropriate description of damping effects should be taken into account.

At this point we can highlight some advantages of the model used in our work with respect to conventional DIM models. Since in our model all interactions are parametrized with physically reasonable functional forms, not only properties of dimers can be used in
fitting the model parameters, but properties of larger clusters too. This gives an implicit way of including many-body features, even when using a 2-body polarization model. Moreover, our model can eventually contain DIM, as it was shown in the study of helium clusters by fitting the diatomic curves of the ground and excited states. However, the parametrized model is not restricted to this information; for instance, if only the diatomic ground state curve is known, still a Hamiltonian can be constructed from that information and possibly from other properties of the dimer or larger clusters. Of course, the quality of both our model and DIM is based on the quality of the inputs. As a limitation of our model we can mention that even when using many-body polarization there are certain interactions that can not be fit simply because the model uses semi-empirical potentials. For instance, we found for helium that it was not possible to fit simultaneously the cation dimer \textit{ab initio} curves and the neutral dimer ground state using the MBP model.

Based on the study of rare gas cation clusters, what other systems can be studied?. We can think of a natural step where the current model can be easily extrapolated and many of the questions about delocalization can gain renewed interest, this is the study of metal cation clusters of the second row such as \( \text{Mg}_N^+ \). Indeed, there has been little study of \( \text{Mg}_N^+ \) clusters for \( N > 7 \). A very simple approach would consider a model for \( \text{Mg}_N^+ \) virtually equivalent to that of \( \text{He}_N^+ \). It appears however, that the inclusion of both \( s \) and \( p \) valence electron should be taken in to account. Still, all this can be incorporated as a one particle (hole) problem, and can be easily built in our model. Is in these systems where questions about delocalization and surface effects will be crucial to understand the evolution of metallic behavior with size.
BIBLIOGRAPHY


APPENDIX A

EIGENSTATES OF Xe$_2^+$

In this appendix we will show the explicit form of the matrix Hamiltonian and solve for its eigenvalues for Xe$_2^+$ for which we have included spin-orbit coupling. The states of Ar$_2^+$ or Ne$_2^+$, for which spin-orbit coupling is less important, can be easily derived setting the coupling constant equal to zero. Having the explicit form of these eigenvalues is useful because they can be used to fit excited state curves and excitation energies obtained from \textit{ab initio} calculations or experiments. This can be particularly useful since it avoids numerical diagonalization to obtain the eigenvalues, making the fitting process more efficient. Even the eigenstates of Xe$_3^+$ can also be obtained by a similar procedure as described below which is also convenient when fitting trimer properties.

Let us assume that the two Xe atoms are on the $z$ axis. The general case assumes that the site energy that corresponds to the hole being localized on a $p_z$ orbital (for both spin up and down) is different from the energy corresponding to the hole localized in a $p_x$ or $p_y$ orbital. Defining these two energies as $e_\sigma$ and $e_\pi$ and the corresponding hopping terms as $t_\sigma$ and $t_\pi$, the matrix Hamiltonian is written as
\[
H = \begin{bmatrix}
  e_\pi & i\delta & \delta & t_\pi \\
  -i\delta & e_\pi & -i\delta & t_\pi \\
  i\delta & e_\pi & i\delta & t_\pi \\
  \delta & i\delta & e_\sigma & t_\sigma \\
\end{bmatrix}, \quad (A.1)
\]

where all empty sites are zero. The order of the basis set used to construct this matrix is that of Eq. B.28 in Appendix B. It is easy to see that this matrix is a direct sum of two \(6 \times 6\) matrices. The symbols in the matrix marked in bold conform one matrix and the rest the elements conform the second matrix. These matrices are the complex conjugate of one another, and therefore have the same eigenvalues. In other words, there are only six distinct eigenvalues, each doubly degenerate. These eigenvalues are, in order of increasing energy,

\[
(A^2\Sigma_{1/2u}) \rightarrow e_1 = \frac{1}{2}(f_1 - g_1) \quad (A.2)
\]

\[
(B^2\Pi_{3/2g}) \rightarrow e_2 = \delta + e_\pi + t_\pi \quad (A.3)
\]

\[
(C^2\Pi_{3/2u}) \rightarrow e_3 = \frac{1}{2}(f_3 - g_3) \quad (A.4)
\]
\((B^2 \Pi_{1/2g}) \rightarrow e_4 = \delta + e_\pi - t_\pi\) \hspace{1cm} (A.5)

\((C^2 \Pi_{1/2u}) \rightarrow e_5 = \frac{1}{2}(f_1 + g_1)\) \hspace{1cm} (A.6)

\((D^2 \Sigma_{1/2g}) \rightarrow e_6 = \frac{1}{2}(f_3 + g_3),\) \hspace{1cm} (A.7)

where we have defined the following

\[
\begin{align*}
  f_1 &= -\delta + e_\sigma + e_\pi - t_\pi - t_\sigma \\
  g_1 &= \sqrt{f_1^2 + 4(2\delta^2 + (\delta - e_\pi + t_\pi)(e_\sigma - t_\sigma))} \\
  f_3 &= -\delta + e_\sigma + e_\pi + t_\pi + t_\sigma \\
  g_3 &= \sqrt{f_3^2 + 4(2\delta^2 + ((\delta - e_\pi - t_\pi)(e_\sigma + t_\sigma))}.
\end{align*}
\]
In this appendix we derive the form of the spin-orbit matrix in Eq. 2.10. The spin-orbit Hamiltonian is

\[ H_{SO} = a \mathbf{S} \cdot \mathbf{L} = a(S_x L_x + S_y L_y + S_z L_z), \]  

(B.1)

where \( \mathbf{S} \) is the spin angular momentum and \( \mathbf{L} \) is the orbital angular momentum. In order to obtain the matrix elements of \( H_{SO} \) in the basis set of \( p \) orbitals, it is convenient to calculate first the matrix elements in the spherical harmonic basis set characterized by the quantum numbers \( l = 1 \) and \( m_l = -1, 0, 1 \). A function in this basis set is denoted as: \( |k, m_l, m_s \rangle \), where \( k \) numerates the atoms, and \( m_l \) and \( m_s \) are quantum numbers for the projection on the \( z \)-axis of \( L \) and \( S \), respectively. \( S_{x,y} \) and \( L_{x,y} \) can be expressed in terms of the lowering and rising operators as follow:

\[ S_x = \frac{S^+ + S^-}{2}, \quad S_y = \frac{S^+ - S^-}{2i}, \]
\[ L_x = \frac{L^+ + L^-}{2}, \quad L_y = \frac{L^+ - L^-}{2i}. \]
Using these operators Eq. B.1 becomes

\[ H_{SO} = \frac{a}{2}(S^+ L^- + S^- L^+ + 2S_z L_z). \] (B.2)

Operating on \(|k, m_l, m_s \rangle\) we have,

\[ H_{SO}|k, m_l, m_s \rangle = \frac{a}{2}[C_s^+(m_s)C_l^-(m_l)|k, m_l - 1, m_s + 1 \rangle + C_s^-(m_s)C_l^+(m_l)|k, m_l + 1, m_s - 1 \rangle + 2m_lm_s|k, m_l, m_s \rangle]. \] (B.3)

The coefficients \(C_{s,l}^\pm\) are defined as follow:

\[ C_l^\pm = \left[ l(l + 1) - m_l(m_l \pm 1) \right]^{1/2} \] (B.4)
\[ C_s^\pm = \left[ s(s + 1) - m_s(m_s \pm 1) \right]^{1/2}. \] (B.5)

In our case, for a Rg\(^+\) system, \(l = 1\) and \(s = 1/2\). Now, let us apply \(|k', m_l', m_s' \rangle\) to \(H_{SO}\) by the left. The first term in Eq. B.3 gives,

\[ C_s^+(m_s)C_l^-(m_l) \times \langle k', m_l', m_s'|k, m_l - 1, m_s + 1 \rangle. \] (B.6)
The second term gives,

$$C_i^+(m_l)C_s^-(m_s) \times \langle k', m'_l, m'_s|k, m_l + 1, m_s - 1 \rangle. \quad (B.7)$$

Finally, the third gives,

$$2m_l m_s \times \langle k', m'_l, m'_s|k, m_l, m_s \rangle. \quad (B.8)$$

Here the spin part can be separated if we note that

$$\langle k', m'_l, m'_s|k, m_l - 1, m_s + 1 \rangle = \langle k', m'_l|k, m_l - 1 \rangle \times \delta_{m'_l m_{s+1}}, \quad (B.9)$$

$$\langle k', m'_l, m'_s|k, m_l + 1, m_s - 1 \rangle = \langle k', m'_l|k, m_l + 1 \rangle \times \delta_{m'_l m_{s-1}}, \quad \text{and} \quad (B.10)$$

$$\langle k', m'_l, m'_s|k, m_l, m_s \rangle = \langle k', m'_l|k, m_l \rangle \times \delta_{m'_l m_s}. \quad (B.11)$$

Since $m_l$ has three possible values and $m_s$ has two, we need to construct a $6 \times 6$ matrix for a given pair of indexes $k$ and $k'$. Let’s define first the following matrix and its elements,

$$A^{kk'}_{m'_l m_l} \equiv C_i^-(m_l)\langle k', m'_l|k, m_l - 1 \rangle. \quad (B.12)$$

The matrix $A^{kk'}$ is related to the overlap matrix within the spherical harmonic basis set,

$$S^{kk'}_{m'_l m_l} = \langle k', m'_l|k, m_l \rangle. \quad (B.13)$$

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Then we have that

\[ A = \sqrt{2} \begin{bmatrix} S_{10} & 0 & S_{1(-1)} \\ S_{(-1)0} & 0 & S_{(-1)(-1)} \\ S_{00} & 0 & S_{0(-1)} \end{bmatrix} \]  \hspace{1cm} (B.14)

In this last equation, we have omitted the superscripts \( k'k \) in both \( A \) and \( S \) for clarity. This matrix assumes the following numeration of the basis functions: \( m_l = 1, -1, 0 \). All the elements of the second column are zero because \( m_l \) cannot be less than -1. Strictly speaking, what makes these elements zero is the coefficient \( C_{l}^{-}(m_l = -1) = 0 \). The rest of the coefficients \( C_{l}^{-} \) are all equal to \( \sqrt{2} \). The term \( C_{s}^{+}(m_s)\delta_{m_s'} m_{s+1} \) that comes from B.6 and B.9 is, in matrix form,

\[ P_A = \begin{bmatrix} 0 & 1 \\ 0 & 0 \end{bmatrix}, \hspace{1cm} (B.15) \]

where the first and second row correspond to the basis functions with \( m_s = 1/2 \) and \( m_s = -1/2 \) respectively. Finally, the matrix form for the term B.6 is the result of the direct product between the orbital part and the spin part, this is

\[ A^{k'k} \otimes P_A \]  \hspace{1cm} (B.16)

Similarly, for the term in B.7 we define the following matrix elements,
\[ B_{m_l m_l}^{kk'} \equiv C_i^+(m_l) \langle k', m_l' | k, m_l + 1 \rangle, \] (B.17)

which gives the matrix,

\[
\mathbf{B} = \sqrt{2} \begin{bmatrix}
0 & S_{10} & S_{11} \\
0 & S_{(-1)0} & S_{(-1)1} \\
0 & S_{00} & S_{01}
\end{bmatrix}
\] (B.18)

and the matrix for the spin part \( C_s^- (m_s) \delta_{m_s} m_{s-1} \),

\[
\mathbf{P}_B = \begin{bmatrix}
0 & 0 \\
1 & 0
\end{bmatrix}
\] (B.19)

Therefore, term B.7 becomes, in matrix form,

\[
\mathbf{B}^{kk'} \otimes \mathbf{P}_B
\] (B.20)

Similarly for the last term (B.8) we define the matrix elements

\[ C_{m_l m_l}^{kk'} \equiv m_l \langle k', m_l' | k, m_l \rangle, \] (B.21)

which gives the matrix
The matrix for the spin part in the term $m_s\delta_{m'_s \, m_s}$ is

$$P_C = \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}. \quad (B.23)$$

Therefore, term B.8 becomes, in matrix form,

$$2C^{k'k} \otimes P_C. \quad (B.24)$$

Finally, collecting B.16, B.20, and B.24 we obtain the spin orbit Hamiltonian matrix connecting atom $k'$ and $k$,

$$\tilde{H}_{SO}^{k'k} = \frac{a}{2} \left[ A^{k'k} \otimes P_A + B^{k'k} \otimes P_B + 2C^{k'k} \otimes P_C \right]. \quad (B.25)$$

Now, let us consider only consider spin-orbit coupling within an atom, that is to assume that all basis functions for all atoms conform an orthonormal set. This is, after all, the assumption used to construct the tight-binding matrix. Therefore, we must set $S_{m'_l \, m_l} = \delta_{m'_l \, m_l}$ in Eqs. B.18, B.19, and B.22 after which we obtain
\[
\tilde{\mathbf{H}}_{SO} = \begin{pmatrix}
\delta & 0 & 0 & 0 & 0 & 0 \\
0 & -\delta & 0 & 0 & \sqrt{2}\delta & 0 \\
0 & 0 & -\delta & 0 & 0 & \sqrt{2}\delta \\
0 & 0 & 0 & 0 & 0 & \delta \\
0 & \sqrt{2}\delta & 0 & 0 & 0 & 0 \\
0 & 0 & \sqrt{2}\delta & 0 & 0 & 0
\end{pmatrix}.
\] (B.26)

where we have defined \( \delta \equiv a/2 \). We need now to express this last matrix in terms of the basis set of the \( p \) orbitals. Let \( e_1 \) be the set of atomic functions constructed with the spherical harmonics:

\[
e_1 = (|1 \uparrow\rangle, |1 \downarrow\rangle, |-1 \uparrow\rangle, |-1 \downarrow\rangle, |0 \uparrow\rangle, |0 \downarrow\rangle),
\] (B.27)

and let \( e_0 \) be the set of atomic functions constructed with \( p \) orbitals:

\[
e_0 = (|p_x \uparrow\rangle, |p_x \downarrow\rangle, |p_y \uparrow\rangle, |p_y \downarrow\rangle, |p_z \uparrow\rangle, |p_z \downarrow\rangle),
\] (B.28)

where \( \uparrow \) represents \( m_s = 1/2 \) and \( \downarrow \) represents \( m_s = -1/2 \). We must now find a matrix \( U \) such that

\[
e_0 = e_1 \cdot U.
\] (B.29)

\( U \) can be easily found by constructing the \( p \) orbitals as linear combination of spherical
harmonics:

\[ |p_x \uparrow\rangle = \frac{1}{\sqrt{2}} [|-1 \uparrow\rangle + |-1 \uparrow\rangle], \quad \text{(B.30)} \]

\[ |p_y \uparrow\rangle = \frac{i}{\sqrt{2}} [(1 \uparrow\rangle + |-1 \uparrow\rangle), \quad \text{(B.31)} \]

and

\[ |p_z \uparrow\rangle = |0 \uparrow\rangle. \quad \text{(B.32)} \]

An equivalent combination is defined for spin down (\(\downarrow\)). Under the definition of \(U\) in Eq. B.29, the matrix representation \(H\) of the spin-orbit Hamiltonian in this new basis set is given by

\[ H_{SO} = U^{-1} \cdot \tilde{H}_{SO} \cdot U. \quad \text{(B.33)} \]

Eq. B.29 can be written also as:

\[ e_0^\dagger = U^\dagger \cdot e_1^\dagger. \quad \text{(B.34)} \]

Thinking the product in Eq. B.34 as a \(6 \times 6\) matrix times a column vector and using Eqs. B.30, B.31, and B.32, we find \(U^\dagger\):
\[ U^\dagger = \begin{bmatrix}
-\frac{i}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \\
0 & -\frac{i}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} & 0 & 0 \\
\frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 \\
0 & \frac{i}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 \\
0 & 0 & 0 & 0 & 0 & 1 
\end{bmatrix}. \quad (B.35) \]

It turns out that \( U \) is an unitarian matrix, this is,

\[ U^{-1} = U^\dagger. \]

Therefore, Eq. B.33 becomes

\[ H_{SO} = U^\dagger \cdot \tilde{H}_{SO} \cdot U. \quad (B.36) \]

Finally, we can construct the explicit form for the spin-orbit matrix in the basis set of \( p \) orbitals:

\[ H_{SO} = \begin{bmatrix}
0 & 0 & i\delta & 0 & 0 & \delta \\
0 & 0 & 0 & -i\delta & -\delta & 0 \\
-i\delta & 0 & 0 & 0 & 0 & i\delta \\
0 & i\delta & 0 & 0 & i\delta & 0 \\
0 & -\delta & 0 & -i\delta & 0 & 0 \\
\delta & 0 & -i\delta & 0 & 0 & 0 
\end{bmatrix}. \quad (B.37) \]
APPENDIX  C

THE DRUDE MODEL FOR Rg$_2$ AND Rg$_2^+$

In this appendix we will derive the explicit form of the matrix $M$ of the Drude Hamiltonian for Rg$_2$ and Rg$_2^+$ and solve for its eigenvalues. Let us consider first Rg$_2$ and set both atoms on the $x$ axis separated by distance $R$. Then, according to Eq. 2.15

$$M_{ij}^{\nu \eta} = \omega \delta_{ij}^{\nu \eta} - \alpha \omega^2 T_{ij}^{\nu \eta}(1 - \delta_{ij}). \quad (C.1)$$

For $T_{ij}$ we will just consider the form in Eq. 2.12 without any damping function, as this only affects very small distances. According to Eq. 2.12, we have that

$$T_{12} = T_{21} = \begin{bmatrix} \frac{2}{R^3} & 0 & 0 \\ 0 & -\frac{1}{R^3} & 0 \\ 0 & 0 & -\frac{1}{R^3} \end{bmatrix}, \quad (C.2)$$

Therefore using Eqs. C.1 and C.2 we obtain
The eigenvalues of $M$ can be easily found in terms of $2 \times 2$ matrices. For instance, elements $M_{12}, M_{14}, M_{44},$ and $M_{41}$ are interconnected only among themselves. Then the six eigenvalues of $M$ are:

\begin{align*}
\lambda_1 &= \omega^2 - \frac{2\alpha \omega^2}{R^3} \\
\lambda_2 &= \omega^2 + \frac{2\alpha \omega^2}{R^3} \\
\lambda_3 &= \omega^2 - \frac{\alpha \omega^2}{R^3} \\
\lambda_4 &= \omega^2 - \frac{\alpha \omega^2}{R^3} \\
\lambda_5 &= \lambda_3 \\
\lambda_6 &= \lambda_4.
\end{align*}

Finally, according to Eq. 2.20 we obtain the Drude energy
\[ D(R) = \frac{\omega}{2} \left[ \sqrt{1 - \frac{2\alpha}{R^3}} + \sqrt{1 + \frac{2\alpha}{R^3}} + 2\sqrt{1 - \frac{\alpha}{R^3}} + 2\sqrt{1 + \frac{\alpha}{R^3}} - 6 \right]. \]  
(C.10)

It is instructive to see the behavior of this last equation assuming that \( \alpha/R^3 \ll 1 \). The first nonzero term in the Taylor expansion of C.10 gives

\[ D(R) = -\frac{3}{4} \frac{\omega \alpha^2}{R^5}, \]  
(C.11)

which shows how the coefficient \( C_6 \) of the dispersion energy \( (-C_6/R^6) \) is related to \( \omega \) and \( \alpha \), this is

\[ C_6 = \frac{3}{4} \frac{\omega \alpha^2}{R^5}. \]  
(C.12)

From Eq. C.10 is easy to see under what conditions the Drude oscillator model fails, this is when

\[ R^3 < 2\alpha. \]  
(C.13)

Let us consider now \( R_{g_2}^+ \), again with both atoms on the \( x \) axis, and let \( \alpha^+ \) and \( \omega^+ \) be the polarizabilities and oscillator frequency respectively of the atom with the charge. The neutral atom (atom 1) is at the origin while the atom with the charge (atom 2) is at \((R,0,0)\). Then the matrix \( M \) becomes

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$$M = \begin{bmatrix}
\omega^2 & 0 & 0 & -\frac{2\sqrt{\alpha'\omega^+}}{R^3} & 0 & 0 \\
0 & \omega^2 & 0 & 0 & \frac{\sqrt{\alpha'\omega^+}}{R^3} & 0 \\
0 & 0 & \omega^2 & 0 & 0 & \frac{\sqrt{\alpha'\omega^+}}{R^3} \\
-\frac{2\sqrt{\alpha'\omega^+}}{R^3} & 0 & 0 & (\omega^+)^2 & 0 & 0 \\
0 & \frac{\sqrt{\alpha'\omega^+}}{R^3} & 0 & 0 & (\omega^+)^2 & 0 \\
0 & 0 & \frac{\sqrt{\alpha'\omega^+}}{R^3} & 0 & 0 & (\omega^+)^2
\end{bmatrix}. \quad (C.14)$$

The eigenvalues and eigenvectors of this matrix can also be obtained in terms of three $2 \times 2$ matrices. To simplify their expressions, let us define the following variables: $\Delta_+ \equiv \omega^2 + (\omega^+)^2$, and $\Delta_- \equiv \omega^2 - (\omega^+)^2$. Then, the eigenvalues are

$$\lambda_1 = \frac{1}{2}(\Delta_+ - \sqrt{\Delta_+^2 + 16\frac{\alpha'\omega^+}{R^6}(\omega^+)^2}) \quad (C.15)$$
$$\lambda_2 = \frac{1}{2}(\Delta_+ + \sqrt{\Delta_+^2 + 16\frac{\alpha'\omega^+}{R^6}(\omega^+)^2}) \quad (C.16)$$
$$\lambda_3 = \frac{1}{2}(\Delta_- - \sqrt{\Delta_-^2 + 4\frac{\alpha'\omega^+}{R^6}(\omega^+)^2}) \quad (C.17)$$
$$\lambda_4 = \frac{1}{2}(\Delta_- + \sqrt{\Delta_-^2 + 4\frac{\alpha'\omega^+}{R^6}(\omega^+)^2}) \quad (C.18)$$
$$\lambda_5 = \lambda_3 \quad (C.19)$$
$$\lambda_6 = \lambda_4. \quad (C.20)$$
According to Eq. 2.20 part of the Drude energy comes from the term

$$\frac{1}{2} \sum_i^6 (\sqrt{\lambda_i} - 3\omega - 3\omega^+).$$

(C.21)

Similarly to the case of $R_{g_2}$, assuming now $\sqrt{\alpha\alpha^+}/R^3 \ll 1$, the Taylor expansion of Eq. C.21 leads to the term

$$\frac{3}{2} \frac{\omega^+}{\omega^+ + \omega^+} \frac{\alpha}{R^6},$$

which identifies the coefficient $C_{6}^+$ of the dispersion energy as

$$C_{6}^+ = \frac{3}{2} \frac{\omega^+}{\omega^+ + \omega^+} \alpha^+.$$

(C.22)

As in the case of neutral atoms, Eq. C.15 provides the condition under which the Drude oscillator model fails, this is when

$$R^3 < 2\sqrt{\alpha\alpha^+}.$$

(C.23)

We need now to calculate the terms $X_i^2/\lambda_i$ which depend on the electric field. According to Eq. 2.18, this requires the eigenvectors of $M$ since these are the columns of the matrix $U$ that diagonalizes $M$. First, let us construct the $3N$ vector $Y$ of Eq. 2.16,

$$Y = \sqrt{\alpha}\omega(E_x, E_y, E_z, 0, 0, 0),$$

(C.24)
where $E_x$, $E_y$, and $E_z$ are the $x$, $y$, and $z$ coordinates of the electric field on atom 1 originated from the charge on atom 2. Since both atoms are on the $x$ axis, $E_y = E_z = 0$ and $E_x = -1/R^2$. Then the $3N$ vector $X$ is

$$X = Y \cdot U,$$  \hspace{1cm} (C.25)

where $U$ is the matrix whose columns are the eigenvectors of $M$. Since only $Y_1$ is nonzero then

$$X_i = -\frac{\sqrt{\alpha \omega}}{R^2} U_{1i}.$$  \hspace{1cm} (C.26)

Because of the form of $M$ in Eq. C.14, it can be shown that only $U_{11}$ and $U_{12}$ are nonzero. These two elements can be expressed in terms of $\lambda_1$ and $\lambda_2$:

$$U_{11} = \frac{\lambda_1 - (\omega^+)^2}{\sqrt{t^2 + (\lambda_1 - (\omega^+)^2)^2}},$$  \hspace{1cm} (C.27)

and

$$U_{12} = \frac{\lambda_2 - (\omega^+)^2}{\sqrt{t^2 + (\lambda_2 - (\omega^+)^2)^2}},$$  \hspace{1cm} (C.28)

where we have defined $t \equiv -2\sqrt{\alpha\omega^+\omega^+}/R^3$. Therefore, we obtain the Drude energy as

$$D(R) = \frac{1}{2} \sum_i \left[ \sqrt{\lambda_i - 3\omega - 3\omega^+} \right] - \frac{1}{2} \frac{\alpha \omega^2}{R^4} \left[ \frac{U_{11}^2}{\lambda_1} + \frac{U_{12}^2}{\lambda_2} \right].$$  \hspace{1cm} (C.29)

Finally, we can see that as $t \to 0$, $\lambda_1 \to \omega^2$, $\lambda_2 \to (\omega^+)^2$, $U_{11} \to (-1)$, and $U_{12} \to 0$. 

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Considering these limits in the last term of Eq. C.29 we obtain the well known polarization energy

\[ -\frac{\alpha}{2R^3}. \]
APPENDIX D

MOLECULAR ORBITALS OF Rg$_2^+$ AND Rg$_3^+$

These following diagrams represent the molecular orbitals of He$_2^+$, He$_3^+$, Ar$_2^+$, and Ar$_3^+$ constructed within a minimal basis set. They show the correspondence between electronic wavefunctions and hole wavefunctions.
He$_3^+$

2Σ$^+_g$

Σ$^+_u$

Σ$^+_g$

electron wavefunctions

hole wavefunctions

Ar$_2^+$

Σ$^+_g$

Π$^+_u$

Π$^+_g$

Σ$^+_u$

electron wavefunctions

hole wavefunctions

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Ar$_3^+$

electron wavefunctions

hole wavefunctions
APPENDIX E

LETTERS OF PERMISSION
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Jose Alejandro Gascon was born in Villa Maria, in the province of Cordoba, Argentina, the 21\textsuperscript{st} of June of 1972. In 1996 he obtained a Licence degree in physics from the Institute of Mathematics, Astronomy and Physics (FAMAF) at the Nacional University of Cordoba graduating with distinction. In 1996 he obtained a research fellowship from the National Committee of Research of Cordoba, working for about two years at FAMAF on computer simulations of metallic nanoparticles. In 1998 he moved to Baton Rouge, Louisiana, to pursue a doctoral degree in chemistry at Louisiana State University where he complements his research with teaching undergraduate courses as a teaching assistant. In 2000 he was awarded for Superior Performance and Productivity in Chemical Research by the Chemistry Department of Louisiana State University. His research interests include Electronic and Structural Properties of Clusters and simulations using Monte Carlo, Molecular Dynamics and Genetic Algorithms. He will receive a doctoral degree in July of 2002. He is a member of the American Chemical Society.