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Relaxed geometries and dipole moments of positron complexes with diatomic molecules.

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Abstract. Relaxed geometries and dipole moments of diatomic molecules interacting with a slow positron are reported as functions of the positron distance to the more electronegative atom. A molecular model for the complex that allows applications to large systems is used. The electron population on the positron is proposed as a weighting function to calculate the average quantities. Results show Self-Consistent-Field quality or better.

1. Introduction
After some controversy [1, 2], it is now well accepted that a slow energy binding positron is able to alter the equilibrium geometries of molecules and, in consequence, their geometry-dependent properties like dipole moments. Some studies in this direction appeared in the recent literature, though restricted to diatomic molecules [3, 4] due to computational obstacles. However the possibility of extending this important study to larger molecules is now opened with the development of the molecular model [5]. In fact, we reported recent applications to positron complexes with the H_2O, CH_3F and CH_3Cl molecules [6]. In that work, however, we limited to present results for relaxed molecular properties as functions of the positron distance.

A relevant progress would be to find a feasible way of averaging the molecular properties over positron distances without having to calculate the (for now unfeasible) positron wavefunction. In the present work we propose the electron population on the positron as a possible weighting function to perform the averages. Application to geometry relaxation of some diatomic molecules, namely XH (X=Li, Na, K) and BeO, display Self-Consistent-Field (SCF) accuracy or better. The relaxed molecular dipole moments are then calculated as well, in view of their relevance to the study of positron interaction with molecules.

2. Procedure
We perform nuclear-mass-dependent-type Born-Oppenheimer electronic calculations already fully described [5, 6]; here we present just the main features of the approach. Electronic orbitals are expanded in basis functions centered on the nuclei and also on the positron, which is taken here as a light nucleus. A positron-mass-dependent kinetic energy term like

\[ - \sum_{i}^{n} \frac{\nabla_{i}^{2}}{2m_{p}} \]  

(1)
is added to the matrix elements of the n-electron Born-Oppenheimer Hamiltonian, whenever these matrix elements involve two basis functions centered on the positron. In Eq. (1) \( m_p \) is the positron mass and the index \( i \) refers to the electrons. Matrix elements of crossing orbitals are kept unchanged. This procedure guarantees that the kinetic energy of all electrons is corrected for the reduced mass effect when they occupy an orbital centered on the positron. Identical terms depending on the nuclear masses can be added as well but they become irrelevant here, in view of the smallness of the positron mass which yields a huge positron correction.

We are then able to map the electronic energy for different configurations of the nuclei-positron systems by following the standard Born-Oppenheimer procedure. Adding to it the repulsion energy of the positive charged particles we thus generate potential energy surfaces (PES) for positron and nuclei motions. For each positron position the molecule is allowed to relax its geometry and, in consequence, the geometry dependent properties. Other typical electronic quantities as populations, dipole moments, etc., are available from the corresponding computational code [7].

The above procedure is equivalent to an adiabatic separation of the positron and electrons motions. But since we keep the positron kinetic energy the only strong condition to be satisfied by this approach is that the PES in question, namely the ground state PES, is isolated from the others (no crossings or pseudo-crossings involved). We noted that this condition hold for all systems we studied so far.

### 3. Results and discussion

Figure 1 shows schematically the framework and relevant coordinates we use. We observed that the positron occupies a kind of lobe orbital centered on the more electronegative atom, H or O. Up to \( \theta = 60 \) degrees, with a fixed \( R_p \), the PES energy is practically insensitive to \( \theta \) for all systems, but starts rising substantially for \( \theta \) approaching 90 degrees. In consequence we found appropriate to neglect the contribution of configurations having \( \theta > 90 \) degrees and also assume axial symmetry around the \( z \) axis. For the alkaline compounds the typical behavior of the electronic density (represented in figures 2 and 3 for \( \text{NaH-}e^+ \)) shows the transference of almost the whole molecular bond to bind \( e^+ \) to H, while for \( \text{BeO-}e^+ \) the electronic density shows no significant change. The global minima of the PES for all systems lie on this axis so that we plot cuts along \( z \) of the PES, the interatomic distances and the Löwdin electronic population [8] on the positron against positron distance, shown in figure 4.

A common behavior for the alkaline compounds is that the interatomic distance increases as the positron approaches and reaches its maximum close to the minimum of the PES, while for \( \text{BeO-}e^+ \) the interatomic distance is again practically insensitive to the positron. This feature allows large relaxation of interatomic distances and properties for the alkaline compounds.

Due to the large mobility of the positron, the PES minima are hardly useful to represent relaxation. In order to do it without calculating the positron wavefunction we need a kind of distribution function to weight geometries and properties in the generation of reliable averages. In this work we consider the Löwdin electronic population \( \eta(R_p) \) on the positron as a candidate to be this function. This quantity, defined as

\[
\eta(R_p) = \sum_{\nu} P_{\nu\nu},
\]

where \( P \) is the density matrix for any MO-LCAO (Molecular Orbital-Linear Combination of Atomic Orbitals) [9] is chosen in view of its better behavior at shorter positron-molecule distance compared to the more traditional Mülliken population [9], as observed in this work.

Any molecular property \( M \) is then evaluated as

\[
<M> = \int \eta(R_p) M(R_p) R^2 dR_p \int \eta(R_p) M(R_p) dR_p.
\]
Figure 1. Schematic representation of the XH-e+ (X = Li, Na e K) complexes. The minima of the PES lie on the z-axis. A similar framework applied to BeO-e+. R_p is the distance of the positron to the H atom and θ is the axial angle.

Figure 2. Charge density of the NaH-e+ complex for R_p = 10a_0.

Figure 3. Charge density of the NaH-e+ complex in the minimum of the PES.

The integrals in Eq. (3) are evaluated numerically on a grid truncated at R_p = 10 a_0 (already at 5 a_0 we verified that the electronic density on the positron becomes negligible).

The electronic populations in figure 4 are considered as weighting functions and the relaxed dipole moment is evaluated for the isolated molecules in the relaxed geometries. This means that for each positron position we obtain the new minimum molecular geometry; in these relaxed geometry we calculate the dipole moment of the isolated molecule. Except for BeO-e+ we observe significant molecular relaxation as the positron approaches. Particularly the dipole moments increase significantly as the positron approaches the minima of the PES. Using Eq. (3) we average internuclear distances and dipole moments, and compare the first ones with sophisticated values obtained in full correlated calculations [3, 10, 11], displayed in Table 1.

As expected, when we just locate the positron on the minimum of the PES the relaxed geometries look too large so that the corresponding dipole moments (both carrying the subscript "min" in the table) are not reliable. Account must be taken to the positron delocalization. This is accomplished first by the calculation of the average values with Eq. (3). We note that for LiH-e+ our result approaches the SCF one, recovering 40% of the relaxation reported in the assumed best calculation of Strasburger [10]. But for the two other molecules our results lie between the
Figure 4. Interatomic distances (XH and BeO), potential energy and electronic population on the positron of the XH-\(e^+\) (X = Li, Na, e K) and BeO-\(e^+\) complexes against positron distance.

SCF and the Configuration Interaction (CI) results from Buenker et al [3]. The corresponding dipole moments increase by about 3-6% relative to the isolated ones as we go from the lighter to the heavier systems. As we did in [6] we evaluate the two quantities, for comparison, also at \(Z_p = Z_{p,\text{min}} + \frac{1}{2}a_{Ps}^o\), a typical distance for positronic systems, where \(a_{Ps}^o = 2a_o\) means the positronium Bohr radius. These quantities are represented in the table by the subscript “ave” and show an improvement relative to the previous ones as we consider the CI results from [3]. Again the dipole moments show an enhancement relative to the unperturbed ones, now of 3-15%. It becomes clear that the study of the binding of a positron to these molecules should take relaxation in account.

As for the BeO-\(e^+\) complex we found no noticeable relaxation, in full agreement with the literature [4], suggesting that the positron binding to this molecule should be explained by its unperturbed dipole moment as well as by the positron affinity of the oxygen atom along.
Table 1. Internuclear distance ($R_{\text{min}}/\alpha_o$) and dipole moment ($\mu_{\text{min}}$/Debye) in the minimum of the PES, electronic population averaged internuclear distance ($\langle R \rangle/\alpha_o$) and dipole moment ($\langle \mu \rangle$/Debye) and internuclear distance ($R_{\text{ave}}/\alpha_o$) and dipole moment ($\mu_{\text{ave}}$/Debye) in the positron averaged position. a Reference [3]. b Reference [10]. c Reference [11].

|     | $R_{\text{min}}$ | $\mu_{\text{min}}$ | $R_{\text{min}}$ | $\mu_{\text{min}}$ | $\langle R \rangle$ | $\langle \mu \rangle$ | $R_{\text{ave}}$ | $\mu_{\text{ave}}$ |
|-----|------------------|---------------------|------------------|---------------------|----------------|----------------|----------------|----------------|
| LiH | 3.012            | 5.858               | 3.045            | 5.90                | 3.209(SCF)$^a$ | 3.391(CI)$^a$  | 3.152          | 6.004          |
|     |                  |                     |                  |                     | 3.448$^b$     |                 | 3.18           | 6.043          |
|     |                  |                     |                  |                     | 3.458$^c$     |                 | 3.209(SCF)$^a$ | 3.391(CI)$^a$  |
| NaH | 3.550            | 6.839               | 3.597            | 6.901$^a$           | 3.63(SCF)$^a$ | 4.115(CI)$^a$  | 3.795          | 7.182          |
|     |                  |                     |                  |                     | 4.115(CI)$^a$ |                 | 4.15           | 7.751          |
| KH  | 4.231            | 8.693               | 4.250$^a$        | 8.618$^a$           | 4.365(SCF)$^a$| 5.063(CI)$^a$  | 4.533          | 9.246          |
|     |                  |                     |                  |                     |                 |                 | 4.90           | 9.977          |

Some speculative considerations on the positron bonding mechanism to polar diatomic molecules ensue from our calculations. The calculated binding energies of the four molecules considered here have magnitudes of $10^{-1}$ eV [3, 10, 11], about two orders of magnitude higher than slow projectile positrons prepared in experiments [12]. So, it seems reasonable that a slow positron will be easily trapped in the molecular potential while it produces a torque on a non-rotating molecule in order to align with the molecular axis in its preferential site, bonded to the more electronegative atom. Both during the bonding process as well as after binding takes place, the molecular relaxation of geometry and properties must be taken in account, as we consider its large incursions allowed by its huge kinetic energy (as compared to the other nuclei). As a matter of fact, the relaxation effects studied here have a static character. This means that once one starts considering the dynamics of the positron-molecule interaction, the molecular vibrations must be taken from the relaxed minimum geometries, instead of the geometries of the isolated molecules; the exception here is BeO-$e^+$. These conclusions affect not only the binding energy considerations but also other features like annihilation rates and low energy cross sections (cases in which the scattering can be described by the PES).

In conclusion, the molecular approach can handle well the problem of molecular relaxation under positron interaction without the computational burden that obstacles the application of full correlated methods. In the applications we obtained a systematic enhancement of the molecular dipole moments of diatomic hydrides subject to positron binding. The electronic population on the positron is proposed as a weighting function to evaluate average molecular quantities over positron positions. On the other hand, the best results obtained with the typical distance $Z_p = Z_{p,\text{min}} + \frac{1}{2} \alpha_o$ suggest that better weighting functions could still be attempted. We will keep investigating this point.

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