Symmetry breaking and symmetry restoring in ions of loosely bound systems

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We present a theoretical analysis of the effects that lead to distortion or symmetry restoration of the nuclear configuration in ions of weakly bound molecular systems and clusters. The vibronic coupling mechanisms involved are reviewed and discussed in terms of simple and general models. Guided by a qualitative characterization of the wave function of a loosely bound system, we study the symmetry determining effects for such ions in terms of first order (Koopmans'), relaxation and correlation distortion energies associated with electron removal from the parent system. Our discussion suggests that the Koopmans' approximation can reasonably be expected to provide a qualitatively correct dependence of the ion energy on nuclear motion. Exceeding these expectations, it is found in numerical applications to the He$_2^+$ and He$_3^+$ ions that the relaxation and correlation energy changes accompanying symmetry breaking tend to cancel exactly. This implies, and we show in practice, that while insufficiently accurate correlation energy estimates may easily lead to incorrect geometries, the inexpensive Koopmans' approximation can often suffice to obtain the correct energy curvature along symmetry breaking coordinates. Further preliminary results for N$_4$ and CO$_2^+$ suggest that these findings have a much wider applicability than anticipated.

I. INTRODUCTION

Symmetry breaking effects in highly symmetric molecules, leading to a distorted equilibrium configuration of the nuclei, are in a number of cases well characterized phenomena, which can be understood by means of very simple theoretical models and can easily be predicted to occur. In the Jahn–Teller effect, for example, degenerate electronic states are split by their coupling through nuclear distortion. Similarly, in the case of core ionization of highly symmetric molecules, symmetry is broken because the gerade and ungerade core hole state pairs interact through a non totally symmetric vibration mode. In these and other cases, the picture is greatly simplified by the presence of two (or very few) degenerate or close lying electronic states which can couple through nuclear motion and this invariably leads to distortion.

The ions of loosely bound systems and clusters constitute a class of systems where symmetry breaking effects are also found to occur. However, in this case, the situation appears considerably more complex since it cannot generally be expected that near degeneracies of electronic states coupled via antisymmetric vibrations will be present. In fact, as we will see, symmetry restoring effects also play an important role in these systems, so that the symmetry of the nuclear configuration often depends on a delicate balance of opposing effects. As a result, the correct prediction of this symmetry may depend crucially on the level of theory employed. Thus, while very accurate theoretical calculations can successfully address these questions for each particular case or series of related molecules, there appears to be a lack of general understanding and predictive models in the theory concerning symmetry breaking and restoring effects in these systems.

On the other hand, despite the apparent complications, the very intuitive notion of a loosely bound system, that is a system bound only through weak correlation effects, should introduce some useful simplifications in a theory of its ionized states. If the Hartree–Fock wave function of the parent systems is unbound, then it should imply that, at least in some range of nuclear coordinates, its orbitals change with the nuclear positions only because of shifting (and reorthonormalization). It is also reasonable to expect that the changes of the charge reorganization as a function of nuclear displacements occurring upon ionization can essentially be described by a mixing within the occupied orbital space. Within this rather simplified picture, it would then follow that all the information concerning the dependence of the ion energy upon nuclear motion is already essentially contained in the occupied orbitals of the parent system. It was one of the main motivations of the present work to study symmetry determining effects in ions of weakly bound systems in the light of the above intuitive simple model. As prototypes of such systems we have chosen to study the He$_2^+$ and He$_3^+$ ion clusters, because they already provide examples where symmetry breaking and symmetry restoring occur at different levels of theory. We will analyze these effects from various viewpoints and within different theoretical frameworks. We will discuss some remarkable results which are amenable to generalization and provide valuable insight and guidance for further theoretical development and applications.

II. THE HE$_2^+$ AND HE$_3^+$ IONS

As mentioned in Sec. I, He$_2^+$ and He$_3^+$ constitute a clear cut example of ions of loosely bound systems where different
TABLE I. Symmetries of the nuclear configurations for the linear He$_4^+$ and He$_6^+$ clusters obtained at the Hartree–Fock and configuration interaction levels.

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<th>CI</th>
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<td>He$_4^+$</td>
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<td>symmetric ($D_{av}$)</td>
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<td>He$_6^+$</td>
<td>symmetric ($D_{av}$)</td>
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Theoretical methods give grossly different results concerning the symmetry of their equilibrium structure. This is visualized in Table I, where the symmetry of the nuclear configuration is reported at the Hartree–Fock (HF) and configuration interaction (CI) levels for the systems in their linear structure. We note here for completeness that while He$_4^+$ is indeed found to be linear at all levels of theory, He$_6^+$ has been reported to have an equilibrium T-shaped structure.

This is, however, unessential for our discussion and all our results and analysis will refer to linear He$_4^+$ and He$_6^+$. As Table I shows, substantial qualitative discrepancies are found for the equilibrium structures of these ions, depending on the level of theory employed. These discrepancies also display an apparently inconsistent trend, which is difficult to reconcile at first sight with any simple charge localization/delocalization mechanism. He$_4^+$ is found to be asymmetric ($C_{av}$) at the HF level and becomes symmetric ($D_{av}$) at the CI level. Exactly the opposite is observed for He$_6^+$, which is predicted to be highly symmetric at HF level but becomes distorted upon inclusion of electron correlation.

An obvious first conclusion that one is compelled to draw from these findings is that, despite the small size of these systems, electron correlation effects appear crucial for even a qualitative description of bonding and structure. In this respect, incidentally, a point is worth remarking which has apparently been overlooked in recent work on some He$_6^+$ clusters: the charge reorganization due to correlation is not described by the mixing of the Hartree–Fock configuration with its singly excited counterparts having a hole in any other occupied orbital. In fact, it is easily shown that the HF wave function, besides being decoupled from these other configurations is already a multiconfiguration self-consistent-field (MCSCF) solution in this configuration space. In this connection, however, an interesting theoretical result, which to our knowledge has not been pointed out previously, is that multiple MCSCF solutions exist in this single hole configuration space, all of them having the same energy (= Hartree–Fock energy). This means that, depending on the technical details of the MCSCF algorithm used, different MCSCF wave functions, with different configuration mixing coefficients and orbital sets, may be reached which, however, do not describe any physical effect beyond the Hartree–Fock level.

The HF structure of He$_4^+$ can be pictorially described as a He$_2^+$ moiety, carrying almost the whole of the positive charge, plus a helium atom electrostatically bound to it. The effect of electron correlation is essentially that of redistributing the charge so that the two terminal helium atoms are equivalent, and a symmetric ($D_{av}$) structure results. For He$_6^+$ the HF and CI structures are again discordant, but this time in the opposite direction: The HF geometry is symmetric, with a central He$_2^+$ group and two longer and equal terminal bonds. Upon inclusion of electron correlation the structure is distorted, one terminal bond shortening and the other becoming longer. In fact, we find that the latter bond tends to become longer and longer as the CI configuration space is enlarged, suggesting that in the full CI limit the collinear path might be dissociative (possibly with an extremely small barrier), leading to a symmetric He$_5^+$ cluster and a separated helium atom. The above situation can consistently be summarized by saying that the most stable structures of the He$_4^+$ and He$_6^+$ clusters are reached when the positive charge is essentially localized over two neighboring atoms at the HF level, and over three atoms at the CI level. This picture is confirmed by a study of He$_6^+$ clusters of larger size. It reflects the generally expected fact that charge is more localized in the HF wave function than in a correlated wave function. Aside from this rationalization, we would like to analyze the symmetry breaking and restoring effects found for He$_4^+$ and He$_6^+$ in a framework which would allow us to gain more insight into the physical mechanisms through which such effects take place.

Symmetry breaking effects like that occurring in He$_4^+$ are common and well understood. The Jahn–Teller effect and other vibronic coupling mechanisms, or the distortion of symmetric core hole states mentioned in Sec. I, are well known examples of such effects. They are usually most usefully interpreted in terms of the coupling of (two) states of different symmetry through some nontotally symmetric nuclear vibration and a vast body of literature exists on the subject. Viewed in this context, by contrast, the ‘symmetry restoring’ correlation effect observed in He$_4^+$ constitutes a rather unusual finding which, to our knowledge, has not been analyzed theoretically so far. It is therefore instructive to compare the vibronic coupling mechanisms involved in the two cases, and this we shall now discuss by means of very simple illustrative models.

III. SYMMETRY BREAKING AND SYMMETRY RESTORING BY VIBRONIC COUPLING

Let us consider the interaction of two unperturbed electronic states as a function of some nontotally symmetric nuclear motion represented by a coordinate $Q_a$. We assume that at $Q_a = 0$ the two states have different symmetry (no coupling) and become of equal symmetry as $Q_a \neq 0$. For definitiveness, without loss of generality, we can specialize our discussion to a $\Sigma_u$ and a $\Sigma_g$ configurations of a linear symmetric $D_{av}$ system. $Q_a$ can then represent an antisymmetric stretching mode, along which the symmetry of the system is lowered to $C_{av}$, the $\Sigma_u$ symmetry is lifted and the two states couple. We assume both states to have an energy minimum at $Q_a = 0$. The situation is represented schematically in Fig. 1(a) (broken lines). For small displacements from $Q_a = 0$ the energy of both states will have a leading quadratic term in $Q_a$, while their coupling will be linear. We can then represent the interaction in the vicinity of $Q_a = 0$ by the following Hamiltonian:

appears, symmetric with respect to $Q_u = 0$. In this case the interaction is symmetry breaking and the nuclear configuration will distort as shown in Fig. 1(a) (full lines). We note incidentally that condition (3) for the double minimum to occur involves the energy separation $\Delta$, the coupling constant and the harmonic frequency of the lower state, but not the frequency of the upper state.

The above very simple two-state model is already entirely adequate to explain the mechanism of distortion in many cases of practical interest. In particular, a very similar transformation has been successfully used to interpret the chemistry and spectroscopy of mixed-valence complexes.\(^7\) In the symmetric core hole state case, as a further example, the $g$ and $u$ core ionized states have an extremely small separation $\Delta$ and lie far apart in energy from other electronic states. In the Jahn–Teller effect the two interacting states have a vanishing separation. In all these cases, a genuine two-state interaction is actually the dominating effect. In the He$^+$ case under present study, and more generally in symmetry breaking effects for ions of loosely bound systems, one cannot identify two SCF states responsible for the symmetry breaking interaction. Our model can nevertheless be thought to apply by imagining the lower unperturbed state to be the $\Sigma_u^-$ Hartree–Fock ground state of He$^+$ and the upper state to be an effective $\Sigma_u$ state, collectively representing the manifold of $\Sigma_u$ excited configurations. The emerging picture, which can be considered completely general, is thus that symmetry breaking arises from a $g/u$ type of interaction, i.e., it results from the dominating effect of $g$ (or $u$) configurations on the $u$ (or $g$) ground state, coupled through nuclear distortion.

Let us now see, again by means of a simple two-state model, how symmetry can be restored through configuration interaction. We now assume the unperturbed lower (ground) state to be initially distorted, showing a symmetric double minimum as a function of $Q_u$. We may suppose this state to arise from a symmetry breaking interaction occurring at a lower level of approximation, e.g., at the molecular orbital level. The upper state has a minimum at $Q_u = 0$ [see Fig. 1(b), broken lines] and we assume that the two states have the same symmetry for all values of $Q_u$. Thus in the case of a system that at $Q_u = 0$ is of $D_{ab}$ symmetry, both states would be, e.g., $\Sigma_u$. We again expand the energy of the states and their coupling to the lowest orders in $Q_u$, which correctly reproduce the relevant features of the problem. The lowest state can thus be represented by an even quartic polynomial (with a negative harmonic term) and the upper state by a parabola. It suffices for our purposes to treat the coupling to zeroth order, i.e., to consider it a constant $c$ along $Q_u$. We therefore arrive at the following Hamiltonian describing the interaction:

$$
\left[ \begin{array}{cc}
\omega Q_u^2 & \lambda Q_u \\
\lambda Q_u & \Delta + \tilde{\omega} Q_u^2 \\
\end{array} \right],
$$

where $\Delta$ is the (positive) separation between the states at $Q_u = 0$, $\omega$ and $\tilde{\omega}$ are positive parameters related to the harmonic frequencies, and $\lambda$ is the linear coefficient of the coupling. The lower eigenvalue of the Hamiltonian (1) reads

$$
E = 1/2 \left\{ (\tilde{\omega} + \omega) Q_u^2 + \Delta - \sqrt{(\tilde{\omega} - \omega)^2 Q_u^4 + 2[(\tilde{\omega} - \omega)\Delta + 2\lambda^2]Q_u^2 + \Delta^2} \right\},
$$

giving the dependence of the energy of the true state upon $Q_u$. It is readily seen that the energy still has a stationary point at $Q_u = 0$. Furthermore, if the $D_{ab}$ separation between the states $\Delta$ is larger than $\lambda^2/\omega$, then the symmetric structure is still a minimum of the lower state and no distortion occurs. On the contrary, provided

$$
\Delta < \lambda^2/\omega
$$

the stationary point at $Q_u = 0$ is a maximum and two mini-
ously sufficient to inspect the second order expansion of the lower eigenvalue:

\[
E = \frac{1}{2} \left\{ \Delta - \sqrt{\Delta^2 + 4\epsilon^2} \right\} + \left[ \frac{\omega - \omega}{\Delta + 4\epsilon} \right] Q^+_e. \tag{5}
\]

Notice that the quartic coefficient of the lower state \( \gamma \) has no influence on the eigenvalue to second order, i.e., the latter results only from the coupling between the harmonic approximation to the two states. From Eq. (5) it is readily derived that for \( Q_e = 0 \) to be a minimum it is required that the harmonic frequency of the upper state be larger (in absolute value) than that of the lower state and that the following condition be satisfied:

\[
\frac{\Delta - f - 1}{\epsilon} < \sqrt{f}
\]

where \( f = \frac{\omega}{\omega_{\gamma}} > 1 \). Under the above conditions the lower energy eigenvalue has a local minimum at \( Q_e = 0 \) and therefore the \( D_{\alpha\beta} \) symmetry can be fully restored through the interaction. Such a case is shown in Fig. 1(b) (full lines).

It should be pointed out that condition (6) only qualifies the stationary point at the origin as a local minimum: it may of course happen (depending on the higher order terms of the energies) that the lower state retains two other (symmetric) minima at \( Q_e \neq 0 \) and these minima can be lower than that at \( Q_e = 0 \). Our simple analysis is obviously restricted to the neighborhood of the origin and aims only at showing the possibility of a symmetry restoring interaction. In this sense condition (6) should be regarded as a necessary condition for this to happen. Although there may exist real cases where the above two-state model already applies with sufficient accuracy, we can make here the same considerations about the nature of the upper state as discussed in the symmetry breaking case, thereby extending the conceptual validity of our model beyond the simple two-state interaction. The upper state can formally be thought of as an effective state representing the totality of unperturbed states of the same symmetry as the ground state. When the interaction between such an effective state and the unperturbed ground state is a dominating effect, symmetry restoring may occur. As opposed to the symmetry breaking case, therefore, symmetry restoring results from a "g/g" (or "u/v")) vibronic coupling, i.e., it involves states which have equal symmetry at all values of \( Q_e \).

It is obviously difficult to use the above description of symmetry breaking and restoring for a quantitative study of the He\(_2^+\) and He\(_3^+\) cases, which are clearly very far away from the two-state approximation. Nevertheless, our vibronic coupling analysis immediately leads us to a very interesting observation: in both the He\(_2^+\) and He\(_3^+\) cases it is the effect of the \( \Sigma_g \) (in \( D_{\alpha\beta} \)) manifold of excited configurations that dominates and determines the symmetry of the ground state. In He\(_2^+\), which has a \( \Sigma_g \) ground state in \( D_{\alpha\beta} \), this leads to a distortion of the nuclear configuration, whereas in He\(_3^+\), which has a \( \Sigma_g \) ground state, symmetry is restored by CI.

**IV. SYMMETRY BREAKING AND SYMMETRY RESTORING BY RELAXATION AND CORRELATION**

As we mentioned in the previous section, a distorted HF structure such as that of He\(_2^+\) might be the result of a symmetry breaking effect taking place in the one-particle orbital space. This leads immediately to the idea of analyzing the effect of the self-consistent field with respect to some lower order unperturbed state. It is then natural to refer to the Koopmans' theorem (KT) energy of He\(_2^+\), obtained as the neutral ground state HF energy \( E_{HF}^N \) minus the outermost orbital energy \( \epsilon \). Thereby we can study the relaxation effects introduced at the Hartree–Fock level as a function of the asymmetric stretching \( Q_e = (R_1 - R_2)/2 \), where \( R_1 \) and \( R_2 \) are the two bond distances in linear He\(_3^+\). We thus partition the energy of the \( N - 1 \) particle system as

\[
E_{N-1} = E_{KT}^{N-1} - E_R - E_C, 
\]

where

\[
E_{KT}^{N-1} = E_{HF}^N - \epsilon
\]

and

\[
E_R = -(E_{HF}^N - E_{KT}^{N-1})
\]

is the relaxation energy. \( E_C \) is, as usual, the (positive) correlation energy of the ion. This procedure also allows a comparison to be made between the relaxation and the symmetry restoring correlation effects, which is particularly interesting in the light of our simple physical picture of ions of weakly bound systems. If the information concerning the dependence of the ion energy upon nuclear coordinates is approximately contained in the HF wave function of the parent molecule, we should indeed expect the Koopmans structure to be undistorted and the corrections to its energy (that is, the sum of the relaxation and correlation energies) to show a relatively weak dependence on the nuclear displacements.

In Table II we have reported the Koopmans, relaxation and (single reference single plus double excitation, SDCI) correlation energies of He\(_2^+\) for small displacements from \( Q_e = 0 \). The basis set used in the calculations is the same as in Ref. 4. The undistorted geometry corresponds to the SCF structure optimized at \( D_{\alpha\beta} \) symmetry \( (R_1 = R_2 = 1.236 \text{ Å}) \). Since we are interested in the relative variation of the energies with distortion, all the energies reported in Table II are relative to their value at \( Q_e = 0 \). The first important result emerging from Table II is that, as anticipated, the KT energy increases with \( Q_e \). Thus, the distortion occurring at the HF level may indeed be interpreted as a relaxation effect. Consequently, we see in Table II that the relaxation energy increases faster with \( Q_e \) than the KT energy, so that the difference between the changes in Koopmans and relaxation energies is negative. The increase in relaxation energy upon distortion may be seen to arise from charge localization: in the undistorted HF wave function the positive charge is essentially delocalized over the three helium atoms. Upon distortion, the charge can effectively localize over the two helium atoms approaching each other, since to a more localized charge there corresponds a larger relaxation energy.

Since the CI structure is undistorted, this immediately
implies that the correlation energy decreases with $Q_a$ and that some extent of cancellation must indeed take place between the changes in relaxation and correlation. What our results in Table II surprisingly show, however, is that this cancellation is essentially exact (to within the numerical accuracy of the calculations) for small displacements and stays practically exact up to quite large distortions ($Q_a = 0.20$ Å). This means that, apart from a constant energy shift, the dependence of the energy of He$_a^+$ on the asymmetric stretching coordinate is given correctly in Koopmans’ approximation. This nearly exact cancellation between the relaxation and correlation distortion energies is one major finding of the present work. As discussed above, based on our intuitive model, we might have expected the dependence of the Koopmans energy upon $Q_a$ to approximate qualitatively the true shape of the energy curve, i.e., to predict correctly the $D_{am}$ symmetry of the He$_a^+$ linear ion. However, the quantitative accuracy of the cancellation between relaxation and correlation contributions obviously exceeds the applicability of this simple picture and calls for a detailed theoretical analysis. In what follows we shall discuss these results in some more detail, present further examples showing that the above effect is by no means accidental, and shall attempt some explanation and generalization.

The results in Table II have been obtained using single reference SDIC calculations. Therefore, a first obvious question that arises is whether and how accurately the cancellation between relaxation and correlation contributions to the distortion energy would persist at higher orders in the correlation energy. Since the quantity of interest here is the change of correlation along $Q_a$, this question cannot be meaningfully answered by using multireference CI, since this procedure cannot ensure a balanced account of the correlation energy changes. Rather, it would be of great importance to assess the extent of cancellation taking place in the full-CI (FCI) limit. Because the basis set used for the single reference CI is too large to perform FCI calculations, we have repeated the calculations on He$_a^+$ including FCI, using smaller 3s and 2s basis sets. The latter have been obtained by (4/1/1) and (5/1) contraction from a primitive 6s set. The results are displayed in Table III. As they show, the relaxation and correlation distortion energies again cancel almost exactly in the 3s basis, and in this case the full CI correlation gives an even better cancellation than the single reference SDIC. In the 2s basis the accuracy of the cancellation generally worsens somewhat, although it clearly persists up to the full CI limit: in all cases the sum of the relaxation and correlation contributions to the distortion is at least an order of

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*The absolute values at $Q_a = 0$ are (in hartree): $E_{K} = -7.740 837 16$, $E_{R} = 0.021 828 26$, $E_{C}^{SDIC} = 0.060 865 40$, $E_{C}^{FCI} = 0.061 573 62$.
magnitude smaller than either term, as well as than the KT distortion energy. It seems clear from the above results that the cancellation between the relaxation and correlation contributions to the distortion energy of He\(_2^+\), although not analytically exact, holds to a very good approximation and should be regarded as a genuine physical phenomenon.

In the attempt to obtain some more insight into this effect, we resort again to our simplified picture of loosely bound systems and their ions and make it somewhat more definite. Although, as previously remarked, we cannot expect to be able to give an analytical explanation of the surprising exactness of the KT energy curvature, we hope nevertheless to clarify some of the essential underlying reasons for this result. A first consideration stems from the following obvious observation: we can, of course, think the relaxation and correlation calculations on the ionic systems as carried out in the basis of the actual HF orbitals of the closed shell parent system, computed at each nuclear configuration. If we truncate this basis to comprise just the occupied orbitals (for the He\(_n^+\) clusters such a basis would coincide in size with a minimal set), then the energy of the hole state would be given exactly by Koopmans' theorem. Upon enlarging the basis to include the virtual orbital space, relaxation and correlation terms appear in the energy of the hole state, which in principle depend on the internal nuclear coordinates. However, it is reasonable to expect that the molecular orbitals of an unbound system have essentially only a trivial dependence on the nuclear displacements. This may be thought to consist in the shift of the underlying atomic orbital (AO) basis (keeping the molecular orbital coefficients unchanged) followed by reorthonormalization, and corresponds to the idea that no real bonding is described by the molecular orbitals. Their variation with the nuclear positions thus consists simply in "following" the nuclear motion. Equivalently, we may say, that the space spanned by the occupied orbitals (and, separately, that spanned by the virtual orbitals) varies in an entirely predetermined way with nuclear coordinates. Under such conditions, we should indeed expect the corrections to the Koopmans energy for the \(N-1\) particle system to be independent of nuclear motion.

To have some quantitative idea of the consistency of the above argument we have computed (using the 4s1p basis set) the overlap matrices between the occupied orbitals of distorted He\(_3\) and He\(_3^+\) and those of the symmetric (\(Q_0 = 0\)) He\(_3\), the latter suitably shifted and reorthonormalized at each value of \(Q_0\). In practice, if

\[
\psi_i = \sum_j C_{ij} \chi_j(0)
\]

are the molecular orbitals of He\(_3\) in terms of the basis functions \(\{\chi_j\}\) at \(Q_0 = 0\), we take the shifted orbitals

\[
\psi_i' = \sum_j C_{ij} \chi_j(Q_0)
\]

having the same expansion coefficients and reorthonormalize them. We note incidentally that this procedure is strictly related to the definition of orthonormal orbital bases which incorporate the geometry dependence of the electronic Hamiltonian.\(^9\) We then use the shifted and reorthonormalized orbitals as basis for the HF calculations on He\(_3\) and He\(_3^+\) at \(Q_0\). The occupied/occupied upper-left blocks of the resulting HF eigenvector matrices provide directly the overlap matrices in question. We can thus define an average overlap as the euclidean square norm of such matrices divided by the number of occupied orbitals. The average overlap at the various stretching parameters are reported in Table IV, together with the energy difference between the converged HF wave function of He\(_3\) and that obtained using the shifted occupied orbitals only. These data confirm beyond doubt that the shifted vectors are very close to the converged SCF vectors and span practically exactly the occupied orbitals space of the distorted neutral cluster up to large \(Q_0\) values. It is fully legitimate to conclude, as we suggested, that the knowledge of the HF orbitals of He\(_3\) at \(Q_0 = 0\) essentially suffices to determine them at all values of \(Q_0\) (at least within the range investigated). This justifies our earlier argument that the \(Q_0\) dependence of the He\(_3^+\) energy is in large measure already contained in the parent He\(_3\) system. It is also interesting to note the large overlap values between the orbitals of He\(_3\) and He\(_3^+\) throughout the stretching range. This is directly related to the fact that the charge reorganization accompanying ionization results largely in a mixing among the occupied orbitals of the parent system alone.

Since we have expected and rationalized the result of Table IV using properties which are characteristic of all loosely bound systems, it seems clear that our findings are not restricted to the He\(_3^+\) case but can be expected to be generally valid for the whole class of such systems.

There is an important aspect of the cancellation between relaxation and correlation stretching energies which is worthwhile to emphasize. From the above discussion, it appears that there may be cases where a not sufficiently accurate evaluation of the correlation energy (or, more precisely, of the correlation part of the distortion energy) would obviously yield a poor cancellation of the relaxation contribution. Conversely, an apparent (large) deviation from exact cancellation may be an indication of a poor estimate of the correlation energy. A spectacular and instructive example of

\[
\begin{array}{|c|c|c|c|}
\hline
Q_0 (\AA) & \Delta E & \text{Neutral} & \text{Ion} \\
\hline
0.0 & 0.0 & 1.0 & 0.994 808 7 \\
0.01 & 0.017 44 & 0.999 998 3 & 0.994 808 7 \\
0.02 & 0.069 82 & 0.999 992 9 & 0.994 808 8 \\
0.03 & 0.157 41 & 0.999 984 0 & 0.994 808 6 \\
0.04 & 0.280 62 & 0.999 971 5 & 0.994 807 9 \\
0.06 & 0.636 42 & 0.999 933 2 & 0.994 803 4 \\
0.08 & 1.143 98 & 0.999 883 2 & 0.994 791 6 \\
0.10 & 1.812 93 & 0.999 814 5 & 0.994 769 3 \\
0.15 & 4.282 40 & 0.999 558 1 & 0.994 656 2 \\
0.20 & 8.140 57 & 0.999 150 1 & 0.994 464 0 \\
\hline
\end{array}
\]
TABLE V. Koopmans' \((E_{K})\), relaxation \((E_{R})\), and correlation \((E_{C})\) distortion energies (in millihartree) for \(\text{He}^{+}\) as a function of the asymmetric stretching coordinate \(Q_{e}\) (41lp basis).

| \(Q_{e}\) (Å) | \(E_{K}\) | \(E_{R}\) | \(E_{K}^{*}\) | \(E_{R} + E_{C}^{*}\) | \(|E_{C}^{*}/E_{R}|\) | \(|(E_{R} + E_{C}^{*})/E_{K}|\) | \(E_{C}^{b}\) |
|---|---|---|---|---|---|---|---|
| 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | ... | ... | 0.0 |
| 0.01 | -0.01279 | 17.38433 | -17.38340 | 0.00093 | 0.9999 | 0.0727 | -25.50533 |
| 0.02 | -0.03112 | 17.54492 | -17.54119 | 0.00373 | 0.9998 | 0.0730 | -25.38315 |
| 0.03 | -0.11485 | 17.68202 | -17.67365 | 0.00837 | 0.9995 | 0.0729 | -25.25730 |
| 0.04 | -0.20374 | 17.79620 | -17.78135 | 0.01485 | 0.9992 | 0.0729 | -25.11703 |
| 0.06 | -0.45568 | 17.95825 | -17.92500 | 0.03325 | 0.9982 | 0.0730 | -24.80635 |
| 0.08 | -0.80359 | 18.03681 | -17.97811 | 0.05870 | 0.9968 | 0.0730 | -24.45603 |
| 0.10 | -1.24326 | 18.03851 | -17.94759 | 0.09092 | 0.9950 | 0.0731 |

*From 4 reference SDCI calculations using the neutral He\(_{2}\) HF orbital basis. The reference set comprises the four single hole configurations.
*From single reference SDCI calculations using the He\(_{2}^{+}\) orbital basis.
*The absolute values at \(Q_{e} = 0\) (in hartree) are: \(E_{K} = -10.351 396 98\), \(E_{R} = 0.016 562 07\), \(E_{K}^{*} = 0.128 878 71\), \(E_{C}^{b} = 0.128 600 50\).

This is provided by the study of the asymmetric stretching of linear He\(_{2}^{+}\). Here we take \(Q_{e} = (R_{1} - R_{2})/2\), where \(R_{1}\) and \(R_{2}\) are the two terminal bond distances, the central one, \(R_{3}\), being fixed. For reasons which will immediately become apparent, we take the undistorted \((Q_{e} = 0)\) structure to correspond to three long (and equal) bond lengths, \(R_{1} = R_{2} = R_{3} = 2.0\) Å. The results of our calculations, again in terms of Koopmans, relaxation and correlation stretching energies are shown in Table V. Two series of CI results are reported, the first one employing the He\(_{2}^{+}\) orbital basis and the second using the neutral He\(_{2}\) orbital basis.

As one immediately notices in the table, the situation is here characterized by a sudden large increase in relaxation and a corresponding large decrease in correlation occurring immediately upon breaking the symmetry of the \(D_{4h}\) structure. This fact is again easily explained in terms of hole localization. In the He\(_{2}^{+}\) HF wave function the positive charge is, for symmetry reasons, equally distributed (mainly) over the two central helium atoms, which are however much farther apart than in the stable He\(_{2}\) molecule. Immediately upon distortion, the symmetry is broken and the charge can localize over one helium atom only, thus causing a large increase in relaxation. Indeed it is found that at \(Q_{e} = 0.01\) Å the charge is localized for more than 92% on only one atom and the relaxation energy is more than twice as large as in the symmetric structure. The decrease in correlation energy indicates, on the other hand, that the correlation effects tend to redistribute the charge. We see, however, that the procedure one would normally follow, namely use the ion SCF orbitals to carry out the CI calculation, gives a very negative correlation stretching energy which largely overcompensates the increase in relaxation and results in a symmetric CI structure. Thus relaxation and correlation effects, although having opposite sign would seem far from efficiently canceling each other. Quite to the contrary, using the fully delocalized neutral He\(_{2}\) orbitals as basis for the CI on He\(_{2}^{+}\), yields a substantially lower CI total energy for the distorted structure, and we see again that the cancellation between relaxation and correlation contributions is restored almost exactly.

In fact, due to the large variations in the individual contributions, this cancellation is even more effective than in the \(\text{He}^{+}\) case previously examined: the sum of the relaxation and correlation stretching energies is (at \(Q_{e} = 0.01\) Å) 4 orders of magnitude smaller than either contribution, and two orders of magnitude smaller than the Koopmans distortion energy. It may be worth remarking that it was the lack of cancellation in the first series of CI results (using the ionic orbital basis) that led us to consider the possibility that the CI calculations were very inaccurate and, after an analysis of the charge distribution, to the use of the unrelaxed orbital basis. Although the more accurate CI data in Table V result from 4 reference SDCI calculations, we note here that already single reference SDCI calculations using the He\(_{2}\) orbital basis provide essentially identical results: for example, at \(Q_{e} = 0.01\) Å the correlation distortion energy is \(-17.383 25\) instead of \(-17.383 40\) millihartree. We have repeated for the He\(_{2}^{+}\) distortion the same analysis of the orbital overlap as described for He\(_{2}\). It is again found that the overlap between the occupied orbital spaces of distorted neutral He\(_{2}\) and of the undistorted structure is practically unity (to five decimal digits at \(Q_{e} = 0.20\) Å!) throughout the whole range of \(Q_{e}\) values used. We further find that the overlap between neutral and ionic occupied HF orbitals is always larger than 0.99. This means that even the drastic charge localization occurring in He\(_{2}^{+}\) at the HF level upon distortion is again essentially describable as a mixing within the neutral occupied orbital space only.

We believe that the results discussed so far justify the conjecture that, under fairly general conditions which at present we are unable to specify analytically, the sum of relaxation and correlation energy of ions of loosely bound systems is almost exactly constant along symmetry breaking nuclear displacements.

V. SUMMARY, FURTHER EXAMPLES, AND CONCLUSIONS

In this work we have studied the theoretical aspects of symmetry breaking and symmetry restoring effects in ions of loosely bound systems. With the help of simple analytical models we have discussed the vibronic coupling mechanisms which lead to distortion of a highly symmetric nuclear configuration or to restoration of high symmetry in an unsym-
metric structure. This analysis shows that while symmetry breaking is due to the coupling of electronic states of different symmetry through nontotally symmetric nuclear modes of vibration (a well known result), symmetry restoring originates from the dependence on nuclear distortion of the interaction between states of the same symmetry. The $\text{He}_3^+$ and $\text{He}_4^+$ linear ion clusters provide real examples where both such effects take place. Our analysis allows us to conclude that both the distortion of the $\text{He}_4^+$ ground state and the $D_{\text{sh}}$ symmetry of the $\text{He}_4^+$ ground state are caused by the effect of the manifold of $\Sigma$g excited states.

The major result of the present work is provided by the study of the distortion energies of $\text{He}_3^+$ and $\text{He}_4^+$ in terms of first order (Koopmans'), relaxation and correlation contributions. It is found that the relaxation and correlation distortion energies cancel each other nearly exactly (in practice, to within the required accuracy of the calculations). This surprising result implies that the energy dependence on symmetry breaking nuclear motions is given quantitatively by the simple first order approximation, is predicted correctly at the Hartree–Fock level of theory, and can only be recovered by sufficiently accurate correlation energy calculations. We have indeed shown that standard routine single reference SDCI calculations on $\text{He}_3^+$ yield correlation distortion energies which largely overcompensate the relaxation contribution and lead to a wrong prediction of the symmetry of the ion. Only more accurate CI calculations recover both the correct geometry and a practically exact cancellation between relaxation and correlation contributions. By resorting to a physically plausible picture of weakly bound systems, we have shown that these results can be qualitatively rationalized and reasonably expected to constitute a general feature of hole states of such systems.

As a conclusion, we would like to address a few preliminary questions which are directly motivated by our present results. First, one should observe that the analysis in terms of Koopmans, relaxation and correlation energies does not in any way make use of the requirement that the "parent" loosely bound system be neutral. It is therefore interesting to investigate electron removal in charged systems, to see if the cancellation effects can actually be generalized to them. As an example, we have carried out some preliminary calculations on $\text{N}_3^-$ and $\text{N}_4^-$ using a 3$s$2$p$ basis set and single reference SDCI. The results at some values of the distortion coordinate (defined as for $\text{He}_4^+$) are shown in Table VI. The bond lengths at $Q_a = 0$ have been obtained by SCF optimization in $D_{\text{sh}}$ symmetry ($R_1 = R_2 = 1.186$ A). What we find also in this case is indeed in line with our previous results. Notice in particular that the Koopmans and HF data predict different symmetries for the nuclear structure of $\text{N}_4^-$ and again the correlation effects restore the Koopmans symmetry. Thus, relaxation and correlation distortion energies have also in this case opposite sign and their sum is negligible compared to the first order distortion energy. The cancellation between relaxation and correlation terms appears to be less accurate at small values of $Q_a$ and improves substantially at larger distortions. We notice, however, that a similar behavior was found in the case of $\text{He}_4^+$ distortion when using the ionic orbital basis in the CI calculations (see Table V). There we have established that the single reference CI in such a basis was inadequate to describe the correlation effects accompanying symmetry breaking, since these tend exactly to counteract the strong charge localization due to relaxation. It is easily seen that this must be particularly true at small $Q_a$ values. We are thus led to ascribe, also in the case of $\text{N}_4^-$, the low accuracy of cancellation near the origin to inadequacy of the CI level of treatment. This emphasizes once again the important fact that the cancellation between relaxation and correlation terms appears to be, under the appropriate conditions, an almost exact effect; which implies the rather sensational conclusion that it may sometimes be necessary to perform extensive and time consuming CI calculations to reproduce this effect accurately and restore the inex- expansively obtained first order distortion energy curvature. Of course, this statement should be taken cautiously at the present state of knowledge: it may happen that the Koopmans energy itself shows a very weak dependence on nuclear distortion. In such a case even the very small correction resulting from the balance between relaxation and correlation effects can be significant in determining the symmetry of the system.

Finally, it seems natural to pose the question of the range of applicability of our results. We have investigated electron removal in some loosely bound systems and our

### Table VI

| $Q_a$ (Å) | $E_{\text{Kt}}$ | $E_R$ | $E_C$ | $E_R + E_C$ | $|E_R/E_C|$ | $(E_R + E_C)/E_{\text{Kt}}$ |
|-----------|---------------|-------|-------|-------------|-------------|------------------|
| 0.00      | 0.00          | 0.0   | 0.0   | 0.0         | 0.0         | 0.0              |
| 0.04      | 2.7221        | 6.6172| 7.7058| 1.0866      | 1.1645      | 0.3999           |
|           |               |       | (-7.336°)| (-0.7193°)| 1.1087°      | 0.2642°          |
| 0.06      | 6.2366        | 10.1461| 10.7509| -0.6048     | 1.0596      | 0.0970           |
| 0.08      | 11.3792       | 13.7044| 14.1526| -0.4482     | 1.0327      | 0.0364           |
| 0.10      | 18.3181       | 17.1578| 17.9287| -0.7709     | 1.0449      | 0.0421           |

*The absolute values at $Q_a = 0$ are (in hartree): $E_{Kt} = 163.049$, $E_R = 0.038 691$, $E_C = 0.304 35$.

*These numbers were obtained using a SDCI with the HF orbitals of the parent closed-shell system ($\text{N}_4^-$). More accurate CI calculations are needed at small distortions (see the text).
TABLE VII. Koopmans' \( (E_{KT}) \), relaxation \( (E_{R}) \), and correlation \( (E_{C}) \) distortion energies (in millihartree) for \( \text{CO}_3^+ \) as a function of the asymmetric stretching coordinate \( Q_s \) (3s2p basis).

| \( Q_s (\text{\AA}) \) | \( E_{KT} \) | \( E_{R} \) | \( E_{C}^{*} \) | \( E_{R} + E_{C} \) | \( |E_{C}/E_{R}| \) | \( |E_{R} + E_{C}|/E_{KT} \) |
|-------------|----------|----------|----------|----------------|----------------|----------------|
| 0.0         | 0.05b    | 0.08b    | 0.0      | 0.0            | \ldots         | \ldots         |
| 0.04        | 2.465 95 | 26.142 34 | -26.150 03 | -0.007 69 | 1.0003 | 0.0031 |
| 0.06        | 5.794 75 | 33.519 37 | -33.082 20 | 0.437 17 | 0.9860 | 0.0754 |
| 0.08        | 10.884 25| 39.827 86 | -39.222 28 | 0.605 58 | 0.9848 | 0.0556 |

*Correlation energy estimates obtained by Davidson correction to the single reference SDCI total energies.

bThe absolute values at \( Q_s = 0 \) are (in hartree): \( E_{KT} = -187.012 391 05 \), \( E_{R} = 0.040 631 25 \), \( E_{C}^{*} = 0.347 425 12 \).

preliminary understanding of the reasons why relaxation and correlation distortion energies cancel to a very large extent relies on the very nature of such systems. It would be interesting, therefore, to obtain information on an ionic state of a strongly bound molecule, where the effect should not be expected to occur with high accuracy. In Table VII we report some results on the asymmetric stretching of the \( \Sigma_{\text{g}} \) ground state of \( \text{CO}_3^+ \). For these calculations a 3s2p basis set\(^{10}\) has been used. The undistorted geometry used is the experimental one\(^{11}\) \( (r_{\text{CO}} = 1.177 \text{ \AA}) \). The correlation energy data shown are obtained using the Davidson correction to the single reference (SDCI) energies, since the latter give an evidently poor estimate of the correlation energy. Very interestingly, even in the case of \( \text{CO}_3^+ \), our results show similar features to those previously discussed. Although the reliability of the correlation energy estimates cannot be assessed with confidence, it appears clearly that substantial cancellation does indeed take place between the relaxation and correlation energy changes upon distortion. It is remarkable, in particular, that the HF calculations again incorrectly predict a distorted structure for \( \text{CO}_3^+ \), whereas the Koopmans energy gives the correct \( D_{\text{o,a}} \) symmetry.

These data seem to indicate that some of the findings discussed in the present work have a much wider generality than could be expected. This appears beyond doubt to be the case, e.g., for the systematic inability of the Hartree–Fock method to correctly predict the symmetry of the nuclear configuration with respect to symmetry breaking modes. Our present results and discussion provide sufficient grounds, furthermore, to surmise that relaxation and correlation changes along symmetry breaking coordinates have opposite sign and tend to cancel each other. The accuracy of this cancellation appears to vary somewhat, reaching practically exactness in ions of weakly bound systems. There are still many open questions concerning the limitations of this surprising phenomenon. For instance, whether it applies as well to other types of symmetry breaking modes (bending modes, torsional modes, etc.). Further work aimed at a deeper understanding of the effects presented here would be very valuable.

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5. P. Tarantelli and L. S. Cederbaum (to be published).