

## On the bonding in doubly charged diatomics\*

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**Summary.** The potential energy of interacting atomic ions  $A^+ + B^+$  often shows a shallow local minimum separated by a broad potential barrier from the dissociation products at much lower energy. Early interpretations of dication potential shapes were based on the similarity of the electronic structure between isoelectronic neutral and ionic species and led to a picture of a chemical bond superimposed on a repulsive Coulomb potential. More recently, barriers in dication potentials have commonly been interpreted as avoided curve crossings involving covalent and ionic structures. In this paper, we demonstrate that the former model is the appropriate one except in cases with very small asymptotic ionic/covalent energy splittings. By deriving dication wavefunctions from their neutral isoelectronic counterparts, we obtain upper bound dication potential curves which show all the characteristic features. By further modeling induction effects, we arrive at an almost quantitative fit of accurate *ab initio* dication potentials. The “chemical bond plus electrostatic repulsion” interpretation of dication interactions also explains why the accurate calculation of potential curves appears to be much more demanding for dications than for isoelectronic neutrals.

**Key words:** Diatomics, doubly charged – Bonding – Potential energy – Dication potentials

### 1 Introduction

Doubly ionized molecules exhibit a number of properties that make them interesting. Diatomic dications, and some larger systems, often possess substantial internal energy in an internuclear coordinate, with the local potential minimum lying high above the adiabatic dissociation asymptote. But dissociation, although strongly exothermic, is often negligible because it requires tunnel-

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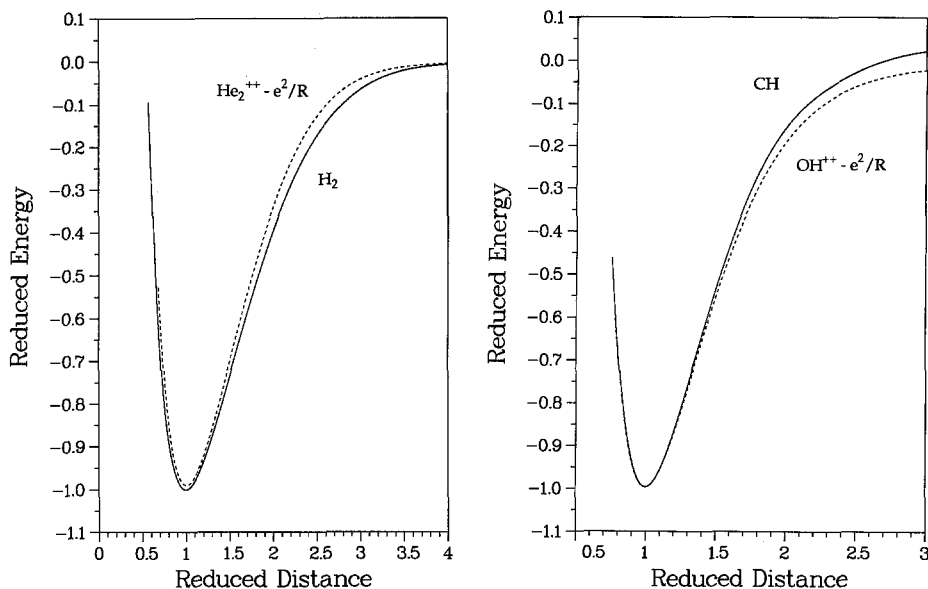
ing through a broad potential barrier that separates the quasi-bound vibrational states from the product continuum. Another interesting feature is that doubly ionized systems can exhibit bonding even when the neutral parents are purely repulsive. The classic example of these effects is  $\text{He}_2^{2+}$  [1], in which metastable vibrational levels lie over 8 eV above the  $\text{He}^+ + \text{He}^+$  dissociation products but are long lived because of an intervening 1.4 eV barrier.

Recently, intense research in this area has uncovered numerous new dications, often by felicitous interplay between measurement and *ab initio* calculations. These recent results provide sufficient data to make observations that seem general to at least diatomic dications.

While any description of small dications must attribute their high energy content to the proximity of incompletely shielded nuclear charges, other properties, like their characteristic broad barriers to dissociation, have evoked various explanations. The model most often referred to in recent literature draws on the common source of barriers in neutral systems, i.e. avoided curve crossings [2–8]. In that model, the barrier and metastability are related to the crossing between the  $A^+ + B^+$  covalent structure, repulsive due to the Coulomb interaction, and a higher lying  $A + B^{++}$  charge transfer (or “ionic”) structure of the same symmetry, attractive because of polarization effects. This picture seems to have gained credibility from the semi-quantitative agreement between observed barrier heights and positions and those calculated from the “avoided crossing – diabatic coupling” model of Gill and Radom [7]. Indeed, such avoided crossings are obvious for dication systems with a small energy separation  $\Delta$  between the asymptotic states  $A^+ + B^+$  and  $A + B^{++}$ , e.g. for  $\text{MgH}^{++}$  (see [5]) and the  $^4II$  excited states of  $\text{OH}^{++}$  [2]. At large internuclear separations, these systems display a sharp crossover from the  $e^2/R$  Coulomb potential to a flat plateau behavior, suggesting little binding is connected with the crossing.

For their model to work in more typical systems with large asymptotic energy separations  $\Delta$  and broad barriers at shorter  $R$ , Gill and Radom [7] required an unphysically large “diabatic coupling” between a covalent and an ionic ( $A + B^{++}$ ) configuration. At the same time, the covalent Heitler–London wavefunction was identified with a pure  $e^2/R$  repulsive potential, thus artificially neglecting the chemical binding one would normally attribute to such a structure. In fact, the relation between covalent and ionic structures in dications is no different from that in neutral molecules. Approximately, the energy separation is  $\Delta - e^2/R$  in both cases: in dications because the lower covalent structure ( $A^+ - B^+$ ) is repulsive, in neutrals because the upper, charge-transfer structure ( $A^- + B^+$ ) is attractive. Moreover, the asymptotic separation  $\Delta$  tends to be unfavorable for interaction in dications, since second ionization energies are generally much larger than the first.

There is little reason to expect electronic structures and binding mechanisms in dications to differ in any significant way from those in the isoelectronic neutrals. Indeed, after subtracting the Coulomb repulsion  $e^2/R$  from reliable theoretical potentials, the remainders look very much like normal neutral molecule potential curves, as shown for sample systems in Figs. 1 and 2. The implication is that the characteristic barrier of dications arises from nothing more than the competition between the  $e^2/R$  repulsion and the exponential onset of a normal chemical bond. In the examples shown, the bond has developed to about 1/3 of its full strength at a nuclear separation corresponding to the top of the barrier and has reached about 2/3 at the minimum.



**Fig. 1.** The potential curves of  $\text{He}_2^{++}$  (dashed) and  $\text{H}_2$  (solid); the dominant long-range term,  $e^2/R$ , has been subtracted from the  $\text{He}_2^{++}$  potential at all geometries, exposing the underlying, mostly chemical, interaction. The reduced coordinates,  $E/D_e$  and  $R/R_e$ , allow for the widely different scales of the two systems. The similarity of the curves shows that, with the Coulomb repulsion removed, the remaining interaction in  $\text{He}_2^{++}$  is the same as that in isoelectronic  $\text{H}_2$ , plus a small long-range term due to induction and higher-order electrostatic effects in the dication. In  $\text{He}_2^{++}$ , the chemical binding shown partially survives the Coulomb repulsion and a local potential minimum develops at an energy high above the asymptote

**Fig. 2.** Similar to Fig. 1, but for  $\text{OH}^{++}$  (dashed) and  $\text{CH}$  (solid). In  $\text{OH}^{++}$ , the chemical binding shown is completely overcome by the Coulomb repulsion of the constituent atomic ions, and no local minimum develops

This “chemical bond plus electrostatic repulsion” picture, underlying much of the earlier work on dications [1, 9–11], has been expressed most clearly by Hurley [9], who uses the virial theorem to predict dication potential curves from those of the isoelectronic neutral species. Although Hurley’s scaling procedure did not yield quantitative agreement, the curves obtained indicated the soundness of the approach. Of course, the similarity of electronic structures of isoelectronic dication and neutral pairs can also be demonstrated directly by comparing the wavefunctions. For the isoelectronic pair  $\text{O}_2$  and  $\text{F}_2^{++}$ , we have shown that the expansion coefficients of the dominant configurations of a CI wavefunction in natural orbitals are almost identical for both molecules, and that ionic structures do not appear differently in the dication [12].

In this paper, we elaborate in some detail on the relation between dication and isoelectronic neutral molecule potential curves. We follow the idea of Hurley and construct a trial wavefunction for the dication by scaling the wavefunction of the neutral partner. Kinetic energy and potential energy terms available from the neutral provide a rigorous upper bound to the dication potentials and describe most of the binding. Including an induction contribution to the poten-

tial accounts for further relaxation of the wavefunction and yields nearly perfect agreement with the dication potentials directly calculated by the same methods used to obtain the neutral molecule data. In this context, we present new *ab initio* calculations of the same type as used in a number of recent studies by this group, i.e. singles and doubles CI with a multiconfiguration reference wavefunction (MR-CI) using large Gaussian bases. The details are identical to those given previously [8, 12–14]. Finally, we discuss the implications of the fact that the barrier in dications is identified with the onset of chemical binding, a region of inherently multiconfigurational character which has received relatively little attention in the context of neutral molecules.

## 2 Scaling procedure

In order to keep the relation between a dication and its isoelectronic neutral as clear as possible, we take advantage of the simplicity of a homonuclear diatomic. In terms of neutral molecule operators for the kinetic energy,  $T$ , the electron nuclear attraction  $V_{\text{en}}$ , and electron-electron repulsion  $V_{\text{ee}}$ , the Hamiltonian of a homonuclear dication may be written as:

$$H^{++} = T + V_{\text{ee}} + (1 + 1/Z)V_{\text{en}} + (Z + 1)^2/R \quad (1)$$

A change of nuclear charge from  $Z$  to  $Z + 1$  is not a small perturbation for first row atoms and can not be treated adequately in first order. As pointed out by Hurley [9], the adjustment of the molecular system to this change is dominantly a uniform contraction of electronic and nuclear distances by some scale factor  $t$ , so that useful upper bounds to the dication energy at internuclear distance  $R$  should be provided by the energy expectation values  $E^{++}(R, t)$  for the trial wavefunctions:

$$\Psi^{++}(R, t) \propto \Psi(r) \quad (2)$$

where  $r = tR$  and  $\Psi(r)$  may be the exact or any approximate wavefunction of sufficient quality. In terms of the neutral molecule expectation values for the kinetic and potential energies at  $r$ , familiar textbook derivations of the virial theorem give:

$$E^{++}(R, t) = t^2 T(r) + t \{ (1 + 1/Z)V_{\text{en}}(r) + V_{\text{ee}}(r) + (Z + 1)^2/r \} \quad (3)$$

The best upper bound is then obtained with a scaling parameter obeying:

$$\partial E^{++}/\partial t = 0$$

$$= t(2 + r \, d/dr)T(r) + (1 + r \, d/dr) \{ (1 + 1/Z)V_{\text{en}}(r) + V_{\text{ee}}(r) + (Z + 1)^2/r \} \quad (4)$$

Of course, if this optimal  $t$  is inserted into Eq. (3) and everything in this equation is expressed in terms of the kinetic and potential energy of the dication, the familiar form of the virial theorem for the dication results.

Given the expectation values and their derivatives for the neutral at some geometry  $r$  – they are readily available from any standard calculation – a rigorous upper bound for the dication energy at  $R$  can be derived from Eqs. (3) and (4). Hurley pointed out that the contraction within an atom is not truly uniform but varies for the different shells, roughly according to the ratio  $Z_{\text{effective}}/(Z_{\text{effective}} + 1)$ , which in turn may limit the quality of the upper bound.

Most of the gain in total energy comes from regions near the nuclei, and the inner shells largely determine the scaling factor as written. But the effects on the desired potential curves are related almost exclusively to the valence shells, and it is more appropriate to use valence shell expectation values in Eqs. (3) and (4) even though this sacrifices the rigorous upper bound. We define valence shell expectation values by subtracting inner shell contributions, determined from atomic fragments stripped of all valence electrons. When applied to neutral atoms, this scaling closely aligns the radial valence charge densities with those of the corresponding ionized atoms (Fig. 3). For all systems discussed below, the scaling factors from Eq. (4) showed variations with internuclear distance of less than one percent, so that equivalent results are obtained by using a fixed scaling factor everywhere.

Figure 4 compares the energy calculated directly for  $F_2^{++}$  with the upper bound energy obtained as described above from isoelectronic  $O_2$  expectation values. The insert shows the same potential curves after subtraction of the  $e^2/R$  repulsion. The data show that the wavefunction obtained by simple scaling of the neutral molecule accounts for most of the dication binding energy. Still, the remaining defect in binding causes a noticeable deviation from the accurate potential curve, in particular with respect to the depth of the well. This sensitivity is due to the close competition between the repulsive  $e^2/R$  component and the attractive binding forces.

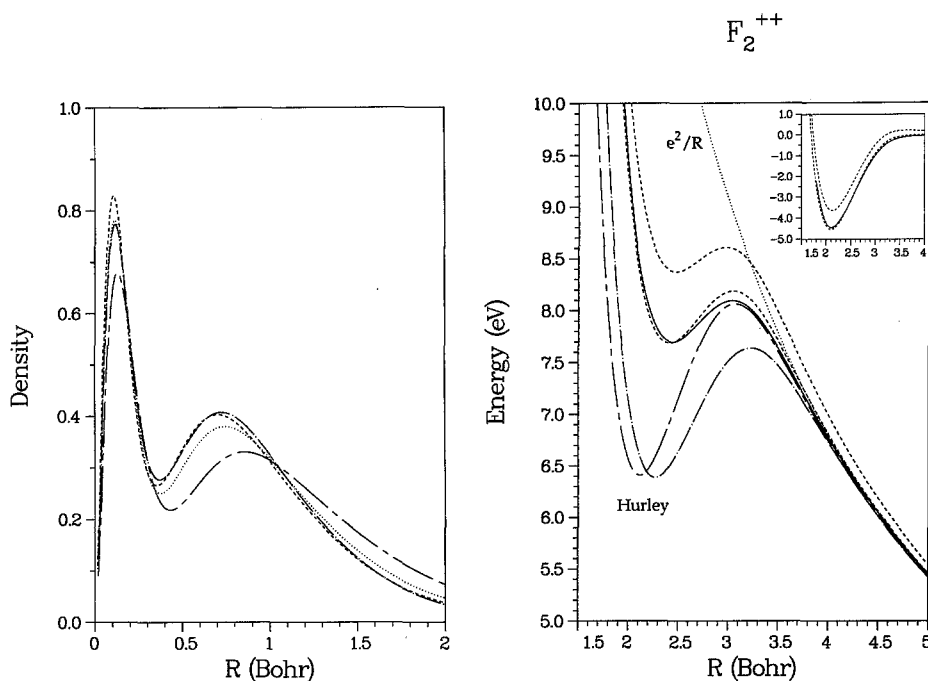
The defect in the binding energy arises from changes in the wavefunction which can not be accounted for by the scaling process. At large internuclear separations, the dominant remaining effect is polarization induced by the partner ion, with an energy contribution of  $-\alpha/R^4$ , where  $\alpha$  is the dipole polarizability of the atomic ion [15]. To model such effects qualitatively for all distances, we use a damped induction potential  $V_{\text{ind}} = -\alpha D(4, \beta R)/R^4$  where  $D$  is the damping function:

$$D(n, \beta R) = 1 - e^{-\beta R} \sum_{i=0, n} (\beta R)^i / i!$$

commonly used in the context of dispersion forces [16]. The dipole polarizability can be easily calculated for the atoms, but higher order effects from quadrupole polarizabilities and dipole hyperpolarizabilities are also relevant because of the strong electric field between the two atomic ions. We incorporated these effects into  $V_{\text{ind}}$  by using an *ad hoc* 15% increment in the dipole polarizability  $\alpha$  [17]. The damping parameter  $\beta$  is poorly defined from physical arguments and was adjusted to fit the dication potential, as scaled from the isoelectronic neutral, to the same potential calculated directly. Figure 4 shows that with the modified  $\alpha$  and single free parameter  $\beta$  the *ab initio* dication potential can be modeled well over its entire range.

### 3 Electronically excited states

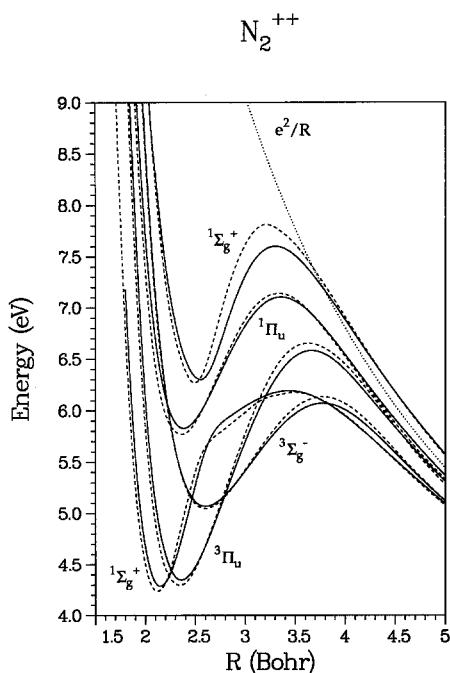
Excited electronic states provide a striking example of the close relation between the isoelectronic neutral and the dication. A particularly interesting example is the pair  $C_2/N_2^{++}$ , in which the two lowest  ${}^1\Sigma_g^+$  states undergo an avoided crossing. For several states of the same symmetry, the wavefunctions of the neutral molecule, after scaling, provide a set of trial functions for which all



**Fig. 3.** The electron density of atomic oxygen (*chain-dash*) and of  $F^+$ ,  $r^2\Psi(r)^2$ , as a function of distance from the nucleus. *Dot-dash*:  $F^+$  density as calculated from an  $F^+$  wavefunction. *Dash*: as derived by scaling the oxygen electron density using a radical scaling factor, 0.82, that interrelates only the valence energies of the two species and preferentially aligns the  $L$ -shells (outer peak); *Dot*: as derived from by scaling the oxygen electron density with a scaling factor, 0.87, that interrelates the total energies of the two species, preferentially aligning the  $K$ -shells (inner peak). The valence-only scaling is expected to be superior in describing chemical bonding

**Fig. 4.** The *ab initio* MR-CI potential energy curve of  ${}^3\Sigma_g^- F_2^{++}$  from Ref. [12] (*solid line*), and several approximations to it. The *dashed curves* were calculated from *ab initio*  $O_2$  properties by using the scaling model described in the text. The *lower dashed curve* includes polarization effects, and shows that dication potential curves can be accurately modeled from isoelectronic neutral data. For comparison, the monotonic dotted curve shows the  $e^2/R$  Coulomb repulsion of the constituent ions, and the lowest two curves show the  $F_2^{++}$  potential as obtained with Hurley's [9] total-energy and valence-only prescriptions. *Insert*: the *solid* and *dashed curves* in the main figure with the  $e^2/R$  contribution removed. The repulsive charge-quadrupole interaction causes the slight barrier near 3.5 Bohr. Even without  $V_{ind}$ , the *upper dashed curve* captures most of the chemical binding; with the addition of  $V_{ind}$ , the *lower dashed curve* is almost indistinguishable from the accurate MR-CI curve

Hamiltonian matrix elements can be obtained from expectation and transition matrix elements for the various potential and kinetic energy terms of the neutral. Diagonalization of this matrix provides nearly rigorous upper bounds to the energies of the dication states. To account for the dependence of  $V_{ind}$  on the diabatic components of an avoided crossing, we first diabatically neutralized the neutral molecule wavefunctions with respect to the dominant expansion coefficient in the CI eigenvectors. Figure 5 shows the remarkable agreement between the resulting potential energy curves and the curves from a direct MR-CI calculation on the



**Fig. 5.** Potential energy curves of several excited electronic states of  $N_2^{++}$ . For each state, the *solid line* is the *ab initio* MR-CI potential calculated as part of this work, and the *dashed line* is the same potential as calculated from our wavefunctions of isoelectronic  $C_2$ , using the model described in the text. The two  $\Sigma$  states of  $N_2^{++}$  retain the notorious avoided crossing found in the ground and first excited states of  $C_2$ . The recovery of this level of detail and the breadth and quality of the agreement across all states demonstrate that the “chemical bond plus electrostatic repulsion” model proposed here works as well for excited states as it does for ground states

dication. The long range splitting of the dication potentials into three distinct groups is due to different quadrupole alignments [18]. The electronic electrostatic moments are inherently present in the neutral (in  $V_{en}$ ) and are scaled with the wavefunction.

Figures 4 and 5 show a systematic overestimation of the dication barrier height. This may be due to promotion of an earlier onset of the chemical bond by the favorable polarization of the charge density, an effect not present in our model.

#### 4 Implications of *ab initio* calculations

The “chemical bond plus electrostatic repulsion” model of dication bonding exposes the fact that the two components of the total energy are typically calculated to different accuracy. The purely electrostatic Coulomb portion is retrieved at full strength in even the crudest *ab initio* calculation. But the remaining chemical bonding potential suffers the errors usually associated with many-electron wavefunctions, where even a large-basis MR-CI may fall short of the true chemical binding. While comfortably small in neutrals, this error is barely tolerable in dications because most of the binding is canceled by the inter-fragment repulsion, leaving the original error as a much greater fraction of the net well depth. The same effect influences the accuracy of calculated spectroscopic constants.

Because of this magnification of the correlation error, the *ab initio* calculation of dication potential curves is much more demanding than calculation of the

corresponding neutral potential. Balancing the adverse effect of the full-strength Coulomb repulsion requires recovery of an anomalously high portion of the correlation energy and forces the simultaneous conscription of all the techniques usually associated with that goal. Large basis sets, including  $g$  functions for first row atoms and  $f$  functions for hydrogen, GVB or MCSCF reference wavefunctions, to properly account for the inherent multiconfiguration nature of the barrier region, and extensive CI all seem essential [8, 13, 19–21]. As has been known since the thorough work of Taylor [19, 20], neglecting any of these elements in dication calculations can lead to unreliable predictions or, in some cases, even unphysical results. Two dications studied enough to provide illustrative examples are  $\text{CH}^{++}$  (see [2, 3, 4, 22–28]) and the  $\text{O}_2^{++}$  ground state [21, 29–31].

## 5 Conclusions

The characteristic shape of most potential energy curves of doubly charged ions, i.e. a local potential minimum separated from the lower dissociation asymptote by a broad barrier, is a result of the competition of a chemical bond and electrostatic repulsion. The similar electronic structure of the ions and the corresponding isoelectronic neutral permits the derivation of almost quantitative ion potentials from expectation values of the neutral species. The binding mechanism places requirements on *ab initio* methods, the most stringent being the proper treatment of the multiconfiguration nature of the dication bond and the recovery of an unusually large fraction of the correlation energy.

Despite the several interpretations of dication bonding, we are pleased to note that Levasseur, Millie, Archirel, and Levy [32] reached conclusions similar to ours in a manuscript that came to our attention after the present work was completed. There now appears to be agreement on bond formation in dications.

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15. Each fragment contributes  $-z^2\alpha/2R^4$  when polarized by the partner ion. For  $A^+ + A^+$ , the sum is  $-\alpha/R^4$ ; for  $A + A^{++}$ , the single term is  $-2\alpha/R^4$
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17. Since the empirical correction to the calculated dipole polarizability is greater than the difference between the parallel and perpendicular components, we applied it to the spherically averaged  $\alpha = (2\alpha_{\perp} + \alpha_{\parallel})/3$
18. The quadrupole of each  $N^+(^3P)$  fragment can be aligned to the partner cation in two ways, attractive when a negative lobe is closest to the partner ion, repulsive when a positive lobe is closest. The quadrupole interaction of two such ions can be attractive-attractive, attractive-repulsive (almost cancelling), and repulsive-repulsive. At long range, the  $N_2^{++}$  potentials approaching the  $N^+(^3P) + N^+(^3P)$  asymptote split into these three groups, with energy contributions of the form  $\gamma Q/R^3$ , with  $\gamma = -1, 1/2, 2$ , and  $Q$  the quadrupole moment
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