



Research Signpost
37/661 (2), Fort P.O., Trivandrum-695 023, Kerala, India

Theoretical Prospect of Negative Ions, 2002: 99-120 ISBN: 81-7736-077-9
Editor: Josef Kalcher

The roles of electrostatics in forming molecular anions and dianions

Jack Simons and Piotr Skurski

Department of Chemistry, University of Utah, 315 South 1400 East, Rm.2020, Salt Lake City, UT 84112

Abstract

In this Chapter, we discuss several classes of anions and dianions for which short-range valence attractive forces are not the only or primary factors in determining the electronic stability. In particular, we examine:

- a. dipole-bound anions in which the long-range charge-dipole potential is crucial;*
- b. quadrupole-bound anions where the underlying neutral has no dipole moment so the shorter-range charge-quadrupole potential may dominate;*
- c. anions formed by attaching an electron to a Rydberg orbital;*
- d. dianions formed by adding two electrons to a dipole-bound orbital;*
- e. dianions formed by attaching two excess electrons to distinct (and often distant) sites;*

Correspondence/Reprint request: Dr. Jack Simons, Department of Chemistry, University of Utah, 315 South 1400 East, Rm.2020, Salt Lake City, UT 84112. E-mail: simons@chemistry.chem.utah.edu

and finally,
f. dianions formed by attaching two electrons to quite proximate sites.

In addition to examining these classes of anions, we also discuss physical models (e.g., the point dipole and fixed finite dipole models and the role of Coulomb repulsions) that are useful in understanding their behavior.

Introduction

If a molecule possesses a vacant or half-filled valence orbital, it may be able to bind an “extra” electron within this orbital to form a stable (with respect to electron detachment) anion. An anion formed in this manner is termed a valence-bound anion. Examples include CN^- in which the extra electron occupies a non-bonding σ orbital; O_2^- where the electron resides in an anti-bonding π^* orbital; ArF^- with the electron in a 2p orbital of F^- van der Waals bound to Ar; $\text{H}_3\text{C-COO}^-$ with the electron in a delocalized π orbital of the carboxylate group, and countless others. Such anions are not a primary subject of this Chapter; instead, we focus attention on:

- anions formed when an electron is bound in a manner that does not involve placing the electron into a valence-type orbital, and
- dianions that may involve electrons attached to valence or non-valence orbitals.

In all of the species we discuss, the interaction of the excess electron(s) with various electrostatic moments of the underlying molecule plays a central role in determining the strength of the electron binding.

This Chapter is not intended to offer a thorough review of the topics it covers; rather, it is intended to survey a wide range of anions and dianions and to provide connections to other Chapters in this book. There are several recent reviews that one can consult to learn more about negative molecular ions in general as well as about several of the classes of anions treated here. These include reviews on gas-phase anions by Kalcher and Sax [1] and by Kalcher [2], on ab initio treatment of anions by Simons and Jordan [3], on anions of polar molecules by Jordan [4], on dipole-bound anions by Gutowski and Skurski [5], on multiply charged anions by Compton [6] and by Scheller, Compton, and Cederbaum [7], and on Double-Rydberg anions by Simons and Gutowski [8].

I. One electron attached to a molecule

In the present Section, we will treat species that arise when one “excess” electron is attached to a non-valence orbital, and, in Section II, we deal with species in which two or more such electrons are attached. In the latter cases, the mutual Coulomb repulsion among the negative charges generates additional complexities in both the experimental and theoretical treatments. Let us now move on to examine the singly charged anion cases.

A. Binding to polar molecules

If a molecule has no empty or half-filled valence orbitals available to bind an electron, then how else might the electron be attracted and bound to the molecule? The answer lies in considering the types of potentials an electron experiences as it approaches a neutral molecule (i.e., in examining the long-range interactions operative

between an electron and a neutral molecule). Because the molecule is neutral, there exists no long-range Coulomb potential (of the form $-qe^2/r$). The potential that has the longest range (i.e., the smallest inverse power of the distance r between the electron and the molecule) is the charge-dipole potential

$$V_{\text{dipole}} = -\boldsymbol{\mu} \bullet \mathbf{r} e / r^3 = -\mu e / r^2 \cos\theta.$$

Here, μ is the dipole moment of the molecule and θ is the angle between the dipole vector $\boldsymbol{\mu}$ and the electron's position vector \mathbf{r} . Of course, there are other potentials whose dependence on r is different. For example, the charge-induced-dipole potential is

$$V_{\text{polariz.}} = -\alpha \bullet \bullet \mathbf{r} r e^2 / 2r^6$$

where α is the polarizability tensor of the molecule and again \mathbf{r} is the position vector of the attached electron, and the charge-quadrupole potential has the form

$$V_{\text{quad}} = -e \mathbf{Q} \bullet \bullet (3\mathbf{r}r - r^2 \mathbf{1}) / 3r^5$$

where \mathbf{Q} is the quadrupole tensor of the molecule and $\mathbf{1}$ is the unit tensor. Of course the \bullet symbol implies the dot product between vectors or tensors.

For any molecule with a non-vanishing dipole moment μ , it is the charge-dipole potential that must be treated first when considering weakly bound electrons because this potential has the longest range. If $\mu = 0$, one must consider the effects of the charge-quadrupole potential, and, if \mathbf{Q} vanishes, one has to look at even shorter-range potentials as possible electron binding sources.

1. The point and fixed finite dipole models

Over fifty years ago, Fermi and Teller [9] and Wightman [10] carried out analyses of the Schrödinger equation

$$(-\hbar^2/2m_e \nabla^2 - \mu e \cos\theta/r^2) \psi = E \psi$$

describing the motion of a single electron of mass m_e in the presence of a purely attractive charge-dipole potential. This is commonly called the point dipole (PD) model because it contains no compensating repulsive potential at small r . The above authors showed that if the magnitude of the dipole moment μ exceeded 1.625 Debyes (or 0.6393 ea_0 , where a_0 is the Bohr radius 0.529 Å and e is the charge of the electron), the potential is strong enough to support bound states of σ symmetry (i.e., having $\exp(i\lambda\phi)$ azimuthal angle dependence with $\lambda = 0$). On the other hand, if $\mu < 1.625$ D, no σ bound states can exist. Even higher critical dipole moments were found to be required to bind π and higher- λ states (e.g., 9.6375 D for π states and 24.218 D for δ states).

Later, Crawford [11] and Dalgarno [12] and Byers-Brown and Roberts [13] among others considered both the point dipole and the fixed finite dipole (FFD) model for one electron moving in the presence of a pure dipole potential. The former model was

discussed above; the latter considers two charges q and $-q$ separated by a distance R to define a dipole moment of magnitude $\mu = qR$ as shown in Fig. 1.

The Schrödinger equation for an electron moving under attraction to the center (A) of charge q and repulsion from center B of charge $-q$

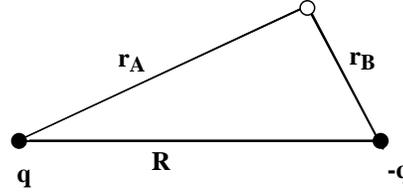


Figure 1. Parameters of the Fixed Finite Dipole Model

$$(-\hbar^2/2m_e \nabla^2 + e q [-1/r_A + 1/r_B]) \psi = E \psi$$

can be rewritten in confocal elliptical coordinates

$$\rho = (r_A + r_B)/R,$$

$$v = (r_A - r_B)/R$$

and the azimuthal angle ϕ . Doing so is appropriate because of the ϕ -independence of the potential and yields

$$\{\partial/\partial\rho[\rho^2-1]\partial/\partial\rho + \partial/\partial v\{1-v^2\}\partial/\partial v + [1/(\rho^2-1) + 1/(1-v^2)] \partial^2/\partial\phi^2 - (\epsilon\rho^2 - \epsilon v^2 + \beta v)\} \psi = E \psi.$$

Here $\epsilon = -m_e R^2 E / 2\hbar^2$, and $\beta = 2m_e R q e / \hbar^2$ are variables that contain the energy E and the dipole moment Rq , respectively. The dependence of ψ on ρ and v can be separated using $\psi = u(\rho) n(v) \exp(i\lambda\phi)$. Doing so produces separate equations for the u and v functions:

$$\partial/\partial\rho[\rho^2-1]\partial u/\partial\rho - \epsilon\rho^2 u - u\lambda^2/(\rho^2-1) + Bu = 0$$

$$\partial/\partial v\{1-v^2\}\partial n/\partial v + (\epsilon v^2 - \beta v)n + n\lambda^2/(1-v^2) - Bv = 0,$$

where B is the separation constant arising when the two-dimensional differential equation is reduced to two one-dimensional equations.

It is important to notice that the variable ϵ depends on both the energy E and the dipole's "length" variable R . In contrast, the variable β is independent of E and depends only on the dipole's magnitude $\mu = qR$ (i.e., only on the product of q and R). Byers-Brown and Roberts noted that these dependences of ϵ and β allow one to conclude that requiring solutions u and n to exist having vanishingly small positive ϵ would place demands on the magnitude of β and thus only on the magnitude of μ , not of R and q separately. In other words, for the FFD model, the conditions for critical electron binding were shown to depend not on R and q separately, but only on their product $qR = \mu$.

Moreover, as discussed in the review by Turner [14], several groups found that the value of μ for which the FFD model barely binds an electron in a σ state is exactly the

same 1.625 D as for the PD model. The critical moments for binding π and δ states in the FFD model are also the same as in the PD model. The main difference between the predictions of the two models lies in the binding energies they predict for $\mu > 1.625$ D. For μ greater than the critical values, the PD model gives infinite binding energy whereas the FFD model gives finite binding (more on the FFD binding energies will be offered later).

Furthermore, it was shown that, even if one adds to the PD or FFD potential any short-range (decaying more rapidly than $1/r^2$) repulsive potential, exactly the same minimum values of μ are needed to critically bind an electron, but the binding predicted in the PD case is no longer infinite.

What do these results have to do with binding electrons to real molecules that contain other electrons and that might be rotating or vibrating? The answer is that, although the PD and FFD models suggest the existence of a critical dipole moment above which electron binding will occur, the quantitative predictions of these models do not fit real molecules very well. As noted above, the PD model predicts that once μ exceeds 1.625 D, an electron will bind in a σ state and the binding energy of this electron will be infinite! Clearly this prediction is incorrect since an infinite binding is unphysical and because one expects the binding energy to depend on the magnitude of the dipole.

For $\mu > 1.625$ D, the FFD model predicts finite binding, but the binding energies it suggests tend to be considerably larger than for real molecules having the same dipole moment. Moreover, an experimental chemist wants to know how large μ must be before significant electron binding (i.e., large enough to render the anion stable enough to be examined and to be within the range of experimental resolution) will occur, but neither model can do this very accurately.

For example, Turner shows [14] that for $\mu = 1.696$ D, the FFD model predicts a binding energy of 10^{-18} eV. However, to achieve a binding energy of 1 cm^{-1} (about as small as could be experimentally probed) with a charge $q = 1$, this model suggests [15] one needs $\mu > 2$ D. It is the latter value that is of more experimental relevance.

Another example of the limitation of the models is provided by KH^- at its equilibrium bond length (2.38 Å) where its dipole moment is 9.465 D. It turns out that LiH^- stretched to $R = 3.2$ Å has the same dipole moment, $\mu = 9.465$ D. Because these species have the same μ values, the FFD model would suggest they have binding energies whose ratio is the square of the inverse ratio of their bond lengths: $E_2/E_1 = (R_1/R_2)^2$. This relationship follows because the ϵ parameter of this model is proportional to ϵR^2 , and it is ϵ that is uniquely determined by μ . The ratio of these two anions' binding energies is $0.35 \text{ eV}/0.90 \text{ eV} = 0.39$, but the ratio of bond lengths squared is $(2.38/3.2)^2 = 0.55$. So, again, we see that the quantitative predictions of the FFD model are not very good.

What is wrong with these models that limits their applicability to realistic molecular systems? Jordan and Luken [16] examined a generalization of the fixed finite dipole model in which one center has charge $Z+q$ and the other center has charge $-q$, and the former center is surrounded by an electron distribution containing Z electrons. This electron distribution's influence on the "extra" electron was approximated in terms of Coulomb and exchange potentials

$$V_{\text{core}} = \sum_{p=1,Z} (J_p - K_p).$$

These potentials, in turn, were expressed in terms of orbitals $\{\phi_j, j = 1, Z\}$ obtained by solving the Hartree-Fock (HF) equations for the Z electrons in the presence of the two centers of charge $Z+q$ and $-q$. Results showed that this modified FFD model could produce electron binding energies more accurately than could the original model. This therefore suggests that the primary deficiencies of the simple PD and FFD models are:

- a. that they ignore Coulomb and exchange repulsion produced by inner-shell electrons;
- b. that they ignore orthogonality of the “extra” electron’s orbital to those of the other electrons in the molecule (this causes the extra electron’s orbital to not have the proper nodal structure);
- c. that they ignore the indistinguishability of the electrons and thus the antisymmetry of the many-electron wave function within which the “extra” electron resides.

So, does this mean that the critical dipole moment suggested by the PD and FFD models is wrong? Not really! It is true that any non-rotating molecule with $\mu > 1.625$ D and any number of inner-shell electrons (i.e., any short-range repulsion) will bind an electron. However, the binding energy may be so small as to be experimentally irrelevant and certainly will depend on the nature of the inner-shell repulsions. In contrast, the modified FFD model discussed immediately above gives more useful approximations to the binding energies of real molecules. More recently, the kind of ideas introduced by Jordan and Luken have been extended and a new model [17] developed in which dipole, quadrupole, and polarization attractions as well as valence repulsions are included.

2. Binding to real molecules

There have been many theoretical and experimental studies of electrons bound to polar molecules in which the binding is ascribed primarily to the charge-dipole attractive potential. Recent reviews [18, 19] offer excellent insight into the current state of affairs of the theoretical studies most of which have been carried out in the laboratories of Drs. Jordan [16,18,20-24], Adamowicz [25-42], Chipman [43], Bartlett [44-46], Gutowski [5,18,23,24,47-55], Desfrancois [56,57], and the two authors [5,18,20,23,24,47-55,58,59]. Much of the early experimental work on dipole-bound anions was produced in the Brauman [60-68], Lineberger [68-75], Desfrancois [76-89], Compton [83,90,91] and Bowen [92-96] laboratories. More recently, the Johnson group [97-107] has also generated a substantial body of data on such anions, and many other experimental and theoretical groups are joining these exciting studies.

In nearly all of these studies, there is good reason to believe that the binding is due primarily to the dipole potential but, in no case can it be shown that the resultant anions are purely dipole-bound. Let us illustrate by examining a few anions that have been termed dipole-bound. The $\text{H}_3\text{C-CN}$ molecule has a dipole moment of 4.34 D and has been shown to form an anion with an electron binding energy of 108 cm^{-1} . Calculations show that the excess electron occupies an orbital localized on the positive end of this dipole within the $\text{H}_3\text{C-}$ group’s “pocket” and rather distant from the underlying molecule’s valence orbitals as shown below in Fig. 2.

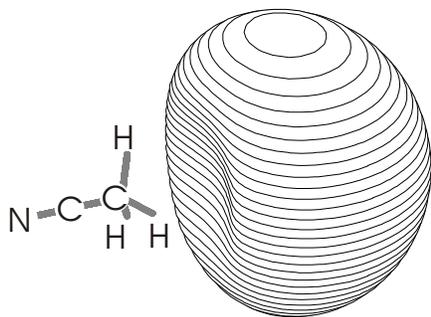


Figure 2. Orbital in which the excess electron resides in $\text{H}_3\text{C-CN}^-$.

Clearly, CH_3CN has no vacant or half-filled valence orbitals that could attach the excess electron (its $\text{CN } \pi^*$ orbital is very high in energy), so it is quite appropriate to call its anion dipole-bound. However, not all molecules having this dipole moment bind an electron to the same extent; for example, H_2CCC also has a dipole moment of 4.34 D but binds by 173 cm^{-1} [102]. So, the binding energy is determined not only by μ but also by the nature of the molecule's other occupied orbitals as reflected in their Coulomb and exchange potentials. Moreover, when one examines the contributions to the electron

binding energy of the $\text{H}_3\text{C-CN}^-$ anion, one finds that the electron-dipole attraction (plus other charge-multipole interactions) combined with the Coulomb and exchange interactions do not reproduce the full electron binding energy. In fact, 57 cm^{-1} or 53 % of the binding arises from the dispersion interaction [23] between the excess electron and the other electrons. Such dispersion contributions have been found to be substantial in many dipole-bound anions. Hence, it is not entirely correct to think of these species as being entirely dipole-bound although the charge-dipole potential is the effect that attracts the excess electron at the longest range.

Let's consider another example- that of acetaldehyde enolate [68] H-COCH_2^- - which has a valence-bound ground state and a dipole-bound excited state. In the ground valence-bound state, the excess electron occupies a delocalized orbital of π symmetry that ranges over the Oxygen and the two Carbon centers. In the excited state, an electron is promoted from this π orbital into an orbital that is bound primarily by the underlying radical's dipole potential. However, again the binding energy of this dipole-bound state is not entirely determined by the radical's dipole moment and the Coulomb and exchange repulsions of the other electrons. Dispersion interactions between the excess electron and the others are important, so again, the anion is not entirely dipole-bound. This example teaches another lesson- that even species such as the $\text{H}_2\text{C-CHO}$ radical that has a half-filled valence orbital can form dipole-bound states if their dipole moments are large enough. That is, the fact that a species forms a valence-bound anion does not preclude it from also forming a dipole-bound state.

A more extreme example of the roles played by shorter-range potentials is offered when one considers anion states of alkali halides or alkali hydrides such as LiF^- or NaH^- , or the alkaline earth analogs such as BeO^- or MgO^- . For example, in neutral LiF , the bonding at the equilibrium internuclear distance is very ionic. Hence, one can view the neutral as a closed-shell F^- anion sitting next to a closed-shell Li^+ cation. Undoubtedly, at very long range, the excess electron is attracted primarily by its dipole interaction with the Li^+F^- . However, in regions of space closer to the Li and F centers, the excess electron experiences both the repulsive Coulomb and exchange interactions mentioned earlier as well as attractive interactions when it is near the Li^+ center, which has an empty 2s orbital. As a result, the excess electron feels the dipole potential at long range but a potential more like that experienced by a Li 2s electron polarized by a

nearby F^- charge. So, in such cases, shorter-range valence potentials combine with the long-range dipole potential to bind the excess electron.

In our opinion, calling an anion state “dipole-bound” reflects the fact that the state exists primarily due to the long-range attractive $-\mu e \cos\theta/r^2$ potential, which produces an orbital localized primarily on the positive side of the molecular dipole and outside the range of the valence orbitals.

3. Summary

The “bottom line” in terms of our understanding of binding an excess electron to polar molecules is that:

- a. Dipole moments considerably in excess of the predictions of the PD and FFD models (1.625 D) are needed before binding exceeds a few cm^{-1} . Experience shows that at least 2.5 D is necessary.
- b. The FFD model overestimates binding energies, but, when Coulomb and exchange potentials of inner shell electrons are included, the model is reasonable but not reliably accurate.
- c. Dispersion interaction of the excess electron with the remaining electrons is usually important to include if one wants accurate results.
- d. Relaxation of the neutral’s orbitals caused by attaching an excess electron is usually small. As a result, a Koopmans’ theorem treatment of the excess electron using specially designed basis sets [103] followed by inclusion of the dispersion interactions [23, 104] between the excess electron and the others is often adequate.
- e. When electron binding energies exceed the spacings between rotational levels of the molecule, it is safe [105] to neglect non-Born-Oppenheimer (non-BO) couplings that can induce electron ejection. Likewise, when the binding energy exceeds vibrational level spacings, it is usually safe to neglect vibrational non-BO couplings that can lead to electron loss.
- f. Even species that form valence-bound anions may also form dipole-bound states if their dipole moments are large enough.
- g. The range of molecules that have been determined to form dipole-bound states is large and growing. In addition to those mentioned above, such states are formed in clusters such as $(\text{H}_2\text{O})_n^-$ and $(\text{HF})_n^-$ [47, 48, 96,106] and in nucleic acid bases such as uracil [32] and thymine [33].

B. Binding an electron to quadrupolar molecules

This subject is dealt with in considerable detail in the Chapter by Prof. Compton, so the present coverage will be rather limited. Here, we will primarily deal with the theoretical differences between dipole and quadrupole binding and mention a few recent attempts to identify species that might be classified as quadrupole-bound.

1. Is there a critical value for the quadrupole moment?

The interaction of an electron with a point quadrupole moment of magnitude Q is governed by the potential

$$V(r,\theta, \phi) = - Qe (3 \cos^2(\theta) - 1)/(3r^3).$$

The Schrödinger equation governing the motion of an electron in this potential is

$$\begin{aligned} &[-\hbar^2/2m_e r^2 \partial/\partial r (r^2 \partial/\partial r) + L^2/2m_e r^2] \psi(r, \theta, \phi) \\ &- Qe (3 \cos^2(\theta) - 1)/(3r^3) \psi = E \psi. \end{aligned}$$

The angular part of the quadrupole potential, which is proportional to the $L = 2$ spherical harmonic, is a quantity that ranges from $-1/3$ to $+2/3$. So, at all points in r, θ, ϕ space, the potential $-Qe (3 \cos^2(\theta) - 1)/(3r^3)$ is less negative than the isotropic potential

$$V^0(r) = -Qe/r^3.$$

Therefore, for any wave function $\psi(r, \theta, \phi)$, the expectation value of the spherical Hamiltonian

$$H^0 = T + V^0$$

will lie below the expectation value of the original Hamiltonian $H = T + V$:

$$\langle H^0 \rangle < \langle H \rangle.$$

The main question is whether bound states of H exist and, if so, for what values of Q .

Landau and Lifschitz [107] demonstrated that, because of the attractive r^{-3} form of the potential and independent of the magnitude of Q , H^0 has bound states of infinitely negative energy in which the electron is bound infinitesimally close to the origin. They speak of the electron “falling” into the origin of the potential. So, unlike the dipole case for which μ has to exceed 1.625 D for bound states to exist, the quadrupole potential can support bound states for any $Q > 0$.

However, neither V nor V^0 is a realistic representation of the electron-molecule interaction as r approaches zero; any real molecule has inner-shell electrons whose repulsions will more than offset the attractive V (or V^0) at small r . Hence, it is of more relevance to consider whether H or H^0 can support bound states but with V or V^0 “cut off” at small r values by a repulsive potential chosen to represent the core and other valence electrons. In this work, we consider the simplest realistic cut off, an infinite “wall” at $r = r_c$. Specifically, we consider the $L = 0$ case of H^0 with the quadrupole V^0 applying for $r > r_c$ and with $V^0 = \infty$ for $r < r_c$. Introducing $\psi = \Phi/r$ into the Schrödinger equation gives the following equation for Φ :

$$-\hbar^2/2m_e \partial^2 \Phi / \partial r^2 - Qe/r^3 \Phi = E \Phi.$$

The function Φ is normalized so that

$$\int_{r_c}^{\infty} \Phi^2 dr = 1$$

and Φ vanishes at $r = r_c$. Let us now try to determine whether this equation can have bound states.

Because the Hamiltonian H^0 is bounded from below (since we cut V^0 off at r_c), we know that the lowest exact eigenvalue of H^0 will

- lie below the expectation value of the above Hamiltonian H^0 taken for any trial function Φ_{trial} and
- lie above the minimum in the potential $-Qe/r_c^3$. We now choose the following trial function [108]

$$\Phi_{\text{trial}} = C(r-r_c)^2 (r-3r_c)^2 \text{ for } r_c < r < 3r_c$$

and $\Phi_{\text{trial}} = 0$ elsewhere, where C is the normalization constant. It can be shown that the expectation value of H^0 for this Φ_{trial} is equal to:

$$\langle \Phi_{\text{trial}} | H^0 | \Phi_{\text{trial}} \rangle = \{ \hbar^2 / 2m_e (656/105) 1/r_c^2 - Qe / r_c^3 \} (315/256),$$

where I is the following positive integral:

$$I = \int_{-1}^1 \frac{(x-1)^4}{(x+2)^3} dx = \int_1^3 \frac{(y-3)^4}{y^3} dy = -56 + 54 \ln 3 = 3.325$$

Because the positive kinetic energy scales as r_c^{-2} and the negative potential energy as r_c^{-3} , it is clear that the total energy can be negative if Q is large enough or r_c is small enough.

This analysis shows that a quadrupole potential of any strength (Q) can bind an electron if the repulsion due to inner shell electrons is weak enough. Conversely, a molecule of any "size" (i.e., having any number of inner-shell electrons) can bind if its quadrupole moment is sufficiently large. Thus, unlike the dipole case, there is no "critical value" for the quadrupole moment.

2. Real molecules that quadrupole bind

As in the case of anions that one says are dipole-bound, it is impossible to find a species for which one can confidently say the excess electron is purely quadrupole bound. For example, the $(\text{BeO})_2^-$ anion considered by Jordan and Liebman [109] and more recently by Gutowski and Skurski [110] has been suggested to be a quadrupole bound anion. At its equilibrium geometry, the neutral $(\text{BeO})_2$ is a rhombus and has zero dipole moment but a quadrupole tensor with principal values of 36.4, 0.4, and $-36.8 \text{ D}\text{\AA}$. In the ground state of the $(\text{BeO})_2^-$ anion, the excess electron is bound by more than 1 eV in an orbital that is shown below.

If one were able to show that a quadrupole potential consistent with the above principal values, cut off by Coulomb and exchange interactions of the inner shell orbitals, would reproduce the above orbital and the 1 eV binding energy, one would have a strong case

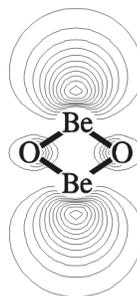


Figure 3. Orbital holding the excess electron in $(\text{BeO})_2^-$

for claiming a dominance of quadrupole binding. However, it is likely that a significant part of the 1 eV binding is due to valence-range attractions in the regions of the two Be^{+2} centers. So, although it is valid to categorize $(\text{BeO})_2^-$ as quadrupole bound because the longest range potential experienced by an excess electron is indeed the charge-quadrupole potential and the d-symmetry charge distribution of the excess electron is consistent with this $L = 2$ potential, there are other potentials that contribute to the binding.

Other molecules that have been suggested to form quadrupole-bound anions include: CS_2 [111], the anti-conformer of succinonitrile ($\text{NC-CH}_2\text{-CH}_2\text{-CN}$) [57], and p-di-nitro-benzene [112]. However, as with $(\text{BeO})_2^-$, it remains difficult to show in a convincing manner that the charge-quadrupole attraction is the dominant contributor to determining the binding energy. For these reasons, we prefer to use the terms dipole-bound and quadrupole-bound to label the longest range potential that contributes to electron binding but to realize that other shorter-range potentials also often play significant roles in determining the total electron binding energy as well as the orbital containing the excess electron.

C. Binding to Rydberg and Zwitterionic sites

Molecules that contain closed-shell cationic sites such as protonated amines R-NH_3^+ and protonated alcohols R-OH_2^+ can bind an electron to form a Rydberg neutral species [113]. In such cases, the long-range Coulomb attraction of the cation site is the dominant contributor to binding, and the repulsions of the inner shell electrons provide the opposing forces. The net result is that the electron is bound to an orbital that is centered on the cation site but has most of its density outside the region where the cation's valence orbitals reside. Two examples of such Rydberg orbitals are shown above.

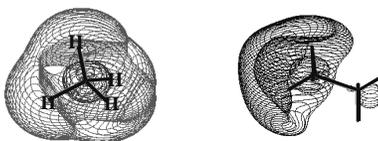


Figure 4. Rydberg orbitals of NH_4 and $\text{H}_3\text{N-CH}_3$

The same Rydberg orbitals that are formed by the Coulomb attraction of the cation site and that attach one electron to form the neutral Rydberg species (e.g., by ca. 4 eV for NH_4 and $\text{H}_3\text{C-NH}_3$) can attach another electron to form so-called [114] double Rydberg anions. In the ground states of these anions, the excess electron is typically bound by only a few tenths of an eV (e.g., by 0.4 eV for NH_4). Moreover, this electron undergoes very correlated motions with the other electron in the Rydberg orbital because the Coulomb repulsions between the two electrons are of the same magnitude as their attractions to the cation center. This means that any successful treatment of such species must allow for a correlated multiconfigurational treatment of at least the two electrons in the Rydberg orbital.

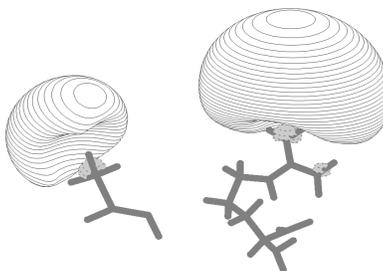


Figure 5. Cation-site orbitals holding the excess electron in anions formed from urea (left) and arginine (right).

Similar cation-site binding occurs in a class of anions formed when an excess electron is attached to the zwitterion tautomers $\text{H}_3\text{N}^+\text{-CHR-COO}^-$ of

molecules such as amino acids. Again, the electron occupies the orbital that is localized primarily on the cation site within the zwitterion neutral. For example, in arginine and urea, the cation-localized orbitals into which the excess electron is attached are as depicted above.

In these zwitterion-derived anions, the binding energy of the excess electron is determined primarily by two factors:

- a. the intrinsic binding strength of the cation site, which is similar to the binding energy in the neutral $\text{H}_3\text{C-NH}_3$ (i.e., 3-4 eV), and
- b. the Coulomb repulsion (e^2/R) exerted on the excess electron by the negatively charged end of the zwitterion, which depends on the distance R between the positive and negative sites (e.g., this is ca. 1.9 eV in arginine and 3.7 eV in urea).

This suggests that the longer the chain separating the two charged sites in the zwitterion, the stronger the net binding energy should be to the cation site. Indeed, such trends are observed here and in numerous other situations where internal Coulomb repulsion plays a crucial role in determining the electron binding energy.

II. Two electrons attached to a molecule

Not surprisingly, to bind two electrons to a single molecule in the absence of stabilizing solvation effects, one must either

- a. have an electron binding site of unusual intrinsic strength or
- b. have two distinct binding sites that are far enough apart.

In either case, the primary obstacle to forming dianions is the mutual Coulomb repulsion between the two excess electrons. For example, two electrons localized 10 Å from one another experience a Coulomb repulsion of 1.4 eV, which can exceed the intrinsic electron binding energy of most sites. Nevertheless, dianions do exist in the absence of solvation, but they often present special challenges to experimental and theoretical study. In this Section, we discuss several classes of dianions that have been subjected to considerable study in recent years.

A. Binding to polar molecules

1. What the PD and FFD models suggest

When the fixed finite dipole (FFD) model is reconsidered for binding two electrons, one faces the following Schrödinger equation [115]:

$$\{-\hbar^2/2m_e (\nabla_1^2 + \nabla_2^2) - q e^2/|\mathbf{r}_1| + q e^2/|\mathbf{r}_1 - \mathbf{R}| - q e^2/|\mathbf{r}_2| \\ + q e^2/|\mathbf{r}_2 - \mathbf{R}| + e^2/|\mathbf{r}_1 - \mathbf{r}_2|\} \psi = E \psi,$$

where q is the charge on the two centers and R is their separation. Introducing scaled electron radial coordinates: $r_1 = \rho_1/q$ and $r_2 = \rho_2/q$ as well as the scaled internuclear distance $R = \rho/q$, transforms the above equation into:

$$q^2 \{-\hbar^2/2m_e (\nabla_1^2 + \nabla_2^2) - e^2/|\rho_1| + e^2/|\rho_1 - \rho| - e^2/|\rho_2| \\ + e^2/|\rho_2 - \rho| + q^{-1} e^2/|\rho_1 - \rho_2|\} \psi = E \psi,$$

where the radial derivatives in ∇^2 now refer to ρ_j derivatives. The Hamiltonian H on the left side of the above equation can be written as:

$$H/q^2 = h(1) + h(2) + q^{-1} e^2/|\rho_1 - \rho_2|,$$

where $h(1)$ and $h(2)$ are the FFD Hamiltonians for the two separate electrons:

$$h(1) = -\hbar^2/2m_e \nabla_1^2 - e^2/|\rho_1| + e^2/|\rho_1 - \rho|,$$

$$h(2) = -\hbar^2/2m_e \nabla_2^2 - e^2/|\rho_2| + e^2/|\rho_2 - \rho|.$$

In the limit, $q \rightarrow \infty$, $R \rightarrow 0$, with $qR = \rho$ finite, H/q^2 becomes $h(1) + h(2)$, so the solutions to

$$(H/q^2) \psi = \epsilon \psi$$

become, in this limit, antisymmetrized products (i.e., Slater determinants) of solutions of the one-electron FFD equation

$$h \phi_j = \epsilon_j \phi_j,$$

multiplied by α or β spin functions. The lowest-energy such solution would be of the form:

$$\psi = |\phi_1 \alpha(\mathbf{r}_1) \phi_1 \beta(\mathbf{r}_2)|,$$

with the vertical lines denoting the Slater determinant. The total energy of this ground-state solution of the two-electron FFD model in the large- q limit is given as the sum of the two energies of the one-electron FFD problem:

$$E/q^2 = 2 \epsilon_1.$$

This shows that as the FFD model approaches the PD limit of large q and small R with fixed qR (n.b., qR is the dipole moment μ), the conditions needed for two electrons to barely bind to form the lowest-energy state are that ϵ_1 be slightly negative. This is exactly the same condition needed for the one-electron PD model to critically bind. Hence, the critical dipole for binding two electrons to the PD is exactly the same as for binding one electron.

In contrast to these findings for the PD model, numerical calculations [115,116] suggest that for the FFD model there is no unique critical $\mu = q R$ value to achieve binding the second electron. Instead, for each q value, there is a critical μ value, and there exists a rather strong dependence of μ_{critical} on q as shown in the figure below.

Although it is difficult to glean from Fig. 6, the large- q limit for μ_{critical} is indeed 1.625 D, as noted earlier. It turns out that there is another asymptote that arises in the FFD model; the minimum value of q for which a bound dianion exists. In this limit, one

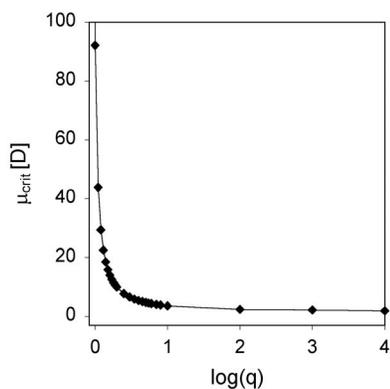


Figure 6. Plot of critical dipole moments for various q values for the FFD model.

repulsion energy e^2/R produced by the other center, where R is the distance to the $-q$ center, and finally

c. determining for what value of R the intrinsic binding energy will be totally offset by the Coulomb repulsion (this value of R is R_c). As we will see later and as discussed in greater detail in the Chapter by Lai-Sheng Wang, competition between intrinsic binding and Coulomb repulsion plays a major role in determining the net stability of multiply charged anions. Recall that the Coulomb repulsion concept also was useful in understanding the binding energies obtained in the zwitterion anions discussed earlier.

has $\mu_{\text{critical}} \rightarrow \infty$ as $q \rightarrow 0.91$. This means that the center with charge $+0.91$ can bind two electrons but only if the other center of charge -0.91 is infinitely far away (and, thus $\mu = qR$ is infinite). For comparison, when $q = 1.0$, two electrons can be bound to the $+q$ center (to form H^-) if the $-q$ center is 19.19 \AA distant (for which $\mu = 92.17 \text{ D}$).

These examples introduce a concept that is important to appreciate when considering the stability of dianions- the role of Coulomb repulsion. It turns out that the critical distance R_c (and hence the critical dipole) for q values in the range $0.91 < q < 2$ can be predicted by:

a. first computing the electron binding energy for the second electron attached to the $+q$ center (this we call the intrinsic binding energy), and then

b. reducing this binding energy by the Coulomb

2. Real cases

To our knowledge, there have been no experimental observations of species that can be classified as dipole-bound dianions. Moreover, there has been only one theoretical prediction [117] of such a dianion, and the structure of this unusual species is shown below.

In this dianion, the second electron is bound by ca. 0.8 eV and resides in the same orbital as does the first excess electron. The relatively large binding energy suggests that, once again, shorter-range attractive potentials also contribute to the binding energy. This, of course, is not surprising considering that the underlying molecule shown above

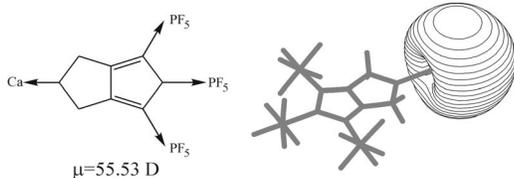


Figure 7. Structure of predicted dipole-bound dianion (left) and of the orbital (right) containing the two excess electrons. This orbital is localized on the Ca end of the molecule.

contains nominally a Ca^{+2} center. It is our hope that in the not-too-distant future, experiments will find such dianions formed by adding two excess electrons to a dipole-binding site.

B. Binding to two distant sites in a single molecule

As discussed above, when considering the possibility of binding two electrons to two distinct sites

(e.g., two orbitals localized far from one another) in a molecule, one must consider the mutual Coulomb repulsion energy between the two anion sites. An excellent illustration of this effect is presented in the photoelectron spectra of dicarboxylate dianions [118] taken in the Wang laboratory (about which one can read much more in Prof. Wang's Chapter). In these spectra (see below), mass-selected dianions are exposed to radiation having more than enough energy $h\nu$ to detach one electron.

The kinetic energy KE of the detached electrons is then subtracted from the photon energy to obtain the electron binding energy $EB = h\nu - KE$. These binding energies are determined for dicarboxylate dianions ${}^{\ominus}\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2^{\ominus}$ having various number of $-\text{CH}_2-$ units.

In Fig. 8, the detachment energies of dianions ${}^{\ominus}\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2^{\ominus}$ of varying length (the Coulomb repulsion is thought to cause the chain to adopt an all-trans geometry in the gas-phase) are plotted as a function of the inverse of the distance r_n between the two carboxylate centers. The linear slope is interpreted in terms of the intrinsic binding energy of a $\text{R}-\text{CO}_2^{\ominus}$ anion (the y-axis intercept of ca. 3 eV) being lowered by the Coulomb repulsion e^2/r_n .

This Coulomb model has proven to be very useful both in interpreting experimental data on such non-proximate dianions [118] and in theoretically predicting binding energies of dianions [119]. For example, we extended earlier studies of dipole binding to LiCN and $(\text{LiCN})_n$ clusters to a model system [120] consisting of two $(\text{LiCN})_2$ units oriented oppositely and separated by an $\text{H}-\text{C}\equiv\text{C}-\text{H}$ "spacer": $(\text{LiCN})_2 \text{H}-\text{C}\equiv\text{C}-\text{H}$ ($\text{NCLi})_2$. We knew that each $(\text{LiCN})_2$ unit would bind an excess electron by 1.35 eV (at the Koopmans' theorem level), and we determined that

- the $(\text{LiCN})_2 \text{H}-\text{C}\equiv\text{C}-\text{H}$ ($\text{NCLi})_2^{-1}$ anion has two nearly degenerate (gerade and ungerade) states that bind the electron by 1.3 eV, which is not surprising based on the above binding energy for $(\text{LiCN})_2^-$;
- the $(\text{LiCN})_2 \text{H}-\text{C}\equiv\text{C}-\text{H}$ ($\text{NCLi})_2^{-2}$ binds its second electron by 0.8 eV.

The 0.5 eV difference between the anion and dianion electron binding energy is consistent with a Coulomb repulsion of two negative charges 29 Å from one another. The distance between the two Li centers in the $(\text{LiCN})_2 \text{H}-\text{C}\equiv\text{C}-\text{H}$ ($\text{NCLi})_2^{-2}$ dianion is 26.2 Å. Clearly, the fact that the centroids of negative charge are displaced somewhat from the Li centers suggests that the Coulomb repulsion is the cause of the 0.5 eV reduction in binding energy when comparing the anion and dianion.

Before closing this sub-section, it is useful to point out a distinction between dipole and quadrupole binding, and the $(\text{LiCN})_2 \text{H}-\text{C}\equiv\text{C}-\text{H}$ ($\text{NCLi})_2$ system offers a good example. In this molecule, we have two oppositely directed highly polar $(\text{LiCN})_2$ units. The entire $(\text{LiCN})_2 \text{H}-\text{C}\equiv\text{C}-\text{H}$ ($\text{NCLi})_2$ molecule has no dipole moment, so it is tempting

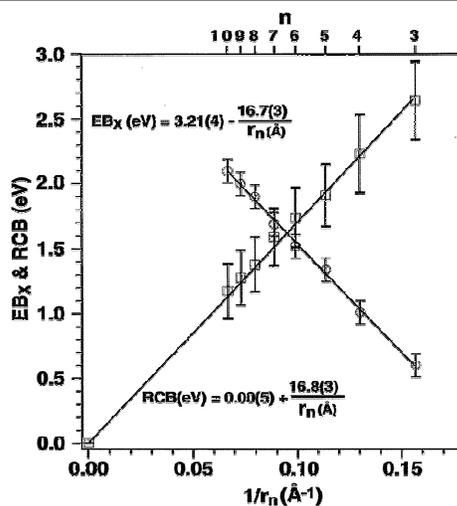


Figure 8. Measured detachment energies of dicarboxylates having various (n) CH_2 units.

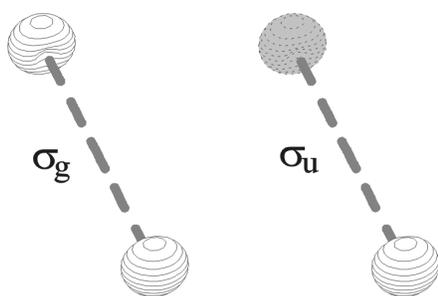


Figure 9. The σ_g and σ_u orbitals of $(\text{LiCN})_2 \text{H-C}\equiv\text{C-H (NCLi)}_2$.

respectively. This means that the left- and right-localized orbitals $L = 2^{-1/2} (\sigma_g + \sigma_u)$ and $R = 2^{-1/2} (\sigma_g - \sigma_u)$ are nearly exact and degenerate eigenstates. Hence, this system really consists of two very weakly interacting dipole-bound systems rather than a quadrupole-bound system.

The lesson this example teaches is that it is important to ask whether an anion claimed to be bound by a moment of order n can more properly be viewed as being locally bound by moments of order $n' < n$ that happen to cancel in the full molecule. As explained, the answer for $(\text{LiCN})_2 \text{H-C}\equiv\text{C-H (NCLi)}_2$ is that the excess electron (s) are dipole-bound. However, in the $(\text{BeO})_2^-$ anion discussed earlier, the authors found a stable anion of 2A_g symmetry (see Fig. 3), but their attempts [110] to identify a corresponding state of ${}^2B_{2u}$ symmetry showed that this state was not electronically stable. That is, the pair of g and u states are split by a very large amount. Hence, for $(\text{BeO})_2^-$, the facts that one does not obtain a nearly degenerate pair of anion states and that the excess electron's orbital extends throughout the entire molecule support calling this a quadrupole-bound anion rather than a dipole-bound anion.

C. Binding to proximate sites

Based on the discussion of Coulomb repulsion presented in earlier Sections, one might wonder if it is possible to form dianions in molecules where the two excess electrons reside in more proximate orbitals. Such systems include many ubiquitous species (e.g., SO_4^{2-} and CO_3^{2-} [119, 121]) as well as more exotic systems [122, 123] (e.g., TeF_8^{2-} [124] and MgF_4^{2-} [125, 126]).

Of course, if the two sites are too close, as they are in O_2^{2-} , the Coulomb repulsion is too large to be offset by the intrinsic binding of each site. However, for the systems listed above and many others, the intrinsic bindings and Coulomb repulsions are close enough to balancing to make such species fascinating to study. Let us consider a few examples.

For tetrahedral MgF_4^{2-} and square antiprism D_{4d} TeF_8^{2-} , the intrinsic binding of the Fluorine ligands as well as the delocalization of the two excess electrons over four or eight equivalent sites, respectively, more than offsets the Coulomb repulsion e^2/R_{LL} (R_{LL} is the ligand-ligand distance). As a result, these dianions are electronically stable by ca. 5 eV and 3 eV, respectively; that is, they bind their second excess electrons by amounts comparable to or in excess of the binding energies of halogens.

to consider its anion a quadrupole-bound anion because the quadrupole moment is the lowest non-vanishing moment of its charge distribution. However, when the orbital into which an excess electron is examined for this case (see below), one sees that this orbital (actually, both the σ_g and σ_u orbitals show this behavior) has a radial extent that is small compared to the entire length of the molecule.

Moreover, one finds two nearly degenerate (i.e., within 4 cm^{-1} [120]) such orbitals of σ_g and σ_u symmetry,

In contrast, for SO_4^{2-} and CO_3^{2-} , the Coulomb repulsion more than offsets the intrinsic binding strengths of the Oxygen ligands, so these dianions turn out to be unstable with respect to electron loss. However, there is more to this interesting competition between Coulomb repulsion and intrinsic valence-range attraction that needs to be discussed.

If one “constructs” any of the dianions mentioned above by bringing a second excess electron toward the corresponding mono-anion, one can imagine what potential this second electron would experience. Certainly, at long range, it would experience Coulomb repulsion caused by the mono-anion’s negative charge. This repulsion would depend on the distance of the second excess electron from the site (s) where the mono-anion’s excess charge is localized. Such long-range repulsive potentials are shown on the right-hand sides of the figure displayed below.

As the second excess electron approaches closer, it eventually enters the region of space where the attractive valence-range potentials (e.g., near the Fluorine or Oxygen ligand orbitals) are strong. In such regions, the total potential will be a sum of these short-range attractions and the Coulomb repulsions. If the former are strong enough, a deep attractive “well” will develop as shown in the top figure, and the dianion will be stable with respect to the mono-anion plus a free electron. Such is the case for TeF_8^{2-} and MgF_4^{2-} .

On the other hand, as for SO_4^{2-} and CO_3^{2-} , if the valence-range attractions are not strong enough, the total potential can display a minimum (as in the lower part of Fig. 10) that lies above the mono-anion plus free electron asymptote. In such cases, the dianion will not be stable, but can be metastable with a substantial lifetime. The lifetimes in such cases are determined by

- the height and thickness of the barrier shown in Fig. 10 (the barriers, in turn, are determined by the maximum Coulomb repulsion), and
- the energy at which the dianion state exists (determined by the intrinsic binding energy minus the Coulomb destabilization).

The lifetimes of such metastable anions have been estimated [119] by

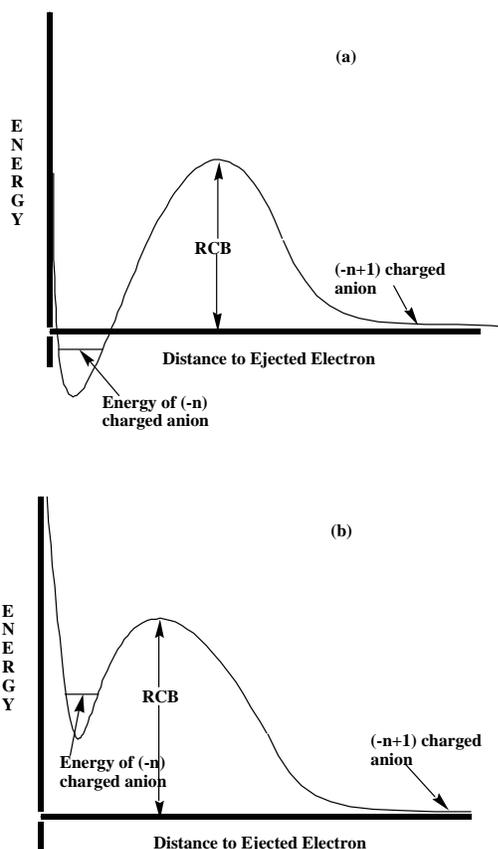


Figure 10. Effective potentials experienced by second excess electron when a stable (top) or metastable (bottom) dianion is formed.

using a simple tunneling model in which the potential parameters shown in Fig. 11 below are:

a. the height of the Coulomb barrier, approximated as e^2/R_{LL} , where R_{LL} is taken to be the ligand-ligand distance;

b. the energy of the dianion relative to that of the mono-anion plus a free electron, approximated as the intrinsic binding energy reduced by the ligand-ligand Coulomb repulsion e^2/R_{LL} ;

c. a straightforward quantum integral is used to compute the probability of escape via tunneling through the Coulomb barrier.

When this kind of model is applied to SO_4^{2-} and CO_3^{2-} , the dianions are predicted to be unstable by 0.75 and 1.50 eV and to have lifetimes of 2.7×10^{-8} and $1.3 \times 10^{-11} \text{ s}^{-1}$, respectively.

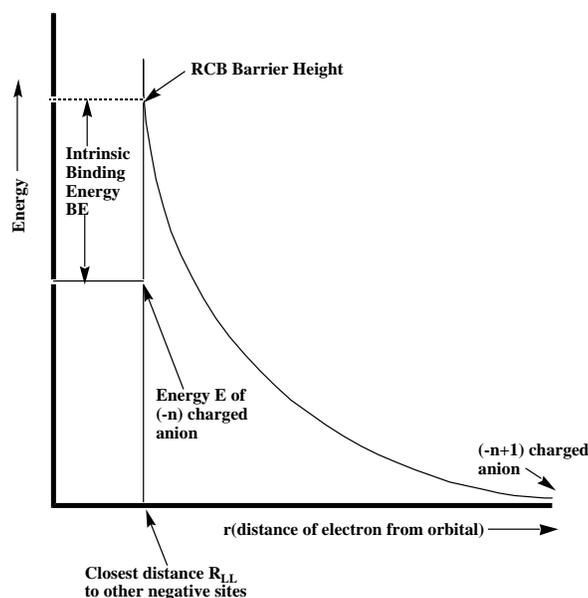


Figure 11. Simple Coulomb barrier model potential in terms of R_{LL} , the ligand-ligand distance and the intrinsic binding energy.

Concluding remarks

In this Chapter, we have attempted to survey several families of anions and dianions whose existence as stable or metastable species depends on one or more of various electrostatic potentials. Included in our treatment have been:

- dipole-bound anions
- quadrupole-bound anions
- double-Rydberg anions and zwitterion anions
- dipole-bound dianions
- dianions formed by valence or dipole binding at distant sites.
- stable and metastable dianions formed by attaching electrons to proximate sites.

It is, of course, possible to imagine anions and dianions formed by combining the above “building blocks” to form clusters. As noted earlier, this has provided an active area of research when two or more molecules with large dipole moments are combined to form such clusters (e.g., $(\text{HF})_n$, $(\text{H}_2\text{O})_n$, etc.). In the limit of a large number of molecules clustered together, one approaches what could be considered a solvated-electron situation. We have chosen, in this Chapter, to not extend our discussion in these directions, but to limit our treatment to the fundamental building blocks that arise when electrostatic effects play dominant roles in electron binding.

Many of the other Chapters in this book deal with some of the same families of anions that we discuss. The entire science of anion chemistry is a rapidly growing

discipline that we believe will continue to attract active attention from both experimental and theoretical groups.

References

1. J. Kalcher and A. F. Sax, *Chem. Rev.* **94**, 2291 (1994).
2. J. Kalcher, *Ann. Reports, Sec. C, Royal Soc. of Chem.* **93**, 147-186 (1996).
3. J. Simons and K. D. Jordan, *Chem. Rev.* **87**, 535 (1987).
4. K. D. Jordan, *Acc. Chem. Res.* **12**, 36 (1979).
5. M. Gutowski and P. Skurski, *Recent Res. Dev. Phys. Chem.* **3**, 245 (1999).
6. R. N. Compton, in *Negative Ions*, V. A. Esaulov, Ed., Cambridge Univ. Press, London (1995).
7. M. K. Scheller, R. N. Compton, and L. S. Cederbaum, *Science*, **270** 1160-1166 (1995).
8. J. Simons and M. Gutowski, *Chem. Rev.* **91**, 669 (1991).
9. E. Fermi, E. Teller, *Phys. Rev.*, 1947, **72**, 399.
10. A.S. Wightman, *Phys. Rev.*, 1950, **77**, 521.
11. O.H. Crawford, *Proc. Roy. Soc. (London)* **91**, 279-284 (1967).
12. O.H. Crawford and A. Dalgarno, *Chem. Phys. Lett.* **1**, 23 (1967).
13. W.B. Brown and R.E. Roberts, *J. Chem. Phys.* **46**, 2006 (1967).
14. J. E. Turner, *Am. J. Physics*, **45**, 758-766 (1977).
15. J. E. Turner, V. E. Anderson, and K. Fox, *Phys. Rev.* **174**, 81 (1968).
16. K.D. Jordan, W. Luken, *J. Chem. Phys.*, 1976, **64**, 2760.
17. H. Abdoul-Carime, Y. Bouteiller, C. Defrancois, L. Philippe, and J. P. Schermann, *Acta Chemica Scandinavia*, **51**, 145 (1997); H. Abdoul-Carime and C. Defrancois, *Eur. Phys. J. D.* **2**, 149 (1998).
18. M. Gutowski, K.D. Jordan, and P. Skurski, *J. Phys. Chem. A* **102**, 2624-2633 (1998).
19. C. Desfrançois, *Phys. Rev. A* **51**, 3667-3675 (1995).
20. K. D. Jordan, K. M. Griffing, J. Kenney, E. L. Andersen and J. Simons, *J. Chem. Phys.* **64**, 4730-4740 (1976).
21. K.D. Jordan and J.J. Wendoloski, *Chem. Phys.* **21**, 145-154 (1977).
22. Y. Yoshioka and K.D. Jordan, *J. Chem. Phys.* **73**, 5899-5900 (1980).
23. M. Gutowski, P. Skurski, A.I. Boldyrev, J. Simons, K.D. Jordan, *Phys. Rev. A*, 1996, **54**, 1906
24. M. Gutowski, P. Skurski, J. Simons, and K.D. Jordan, *Int. J. Quantum Chem.* **64**, 183-191 (1997).
25. L. Adamowicz and E.A. McCullough, *Chem. Phys. Lett.* **107**, 72-76 (1984).
26. L. Adamowicz and E.A. McCullough, Jr., *J. Phys. Chem.* **88**, 2045-2048 (1984).
27. L. Adamowicz and R.J. Bartlett, Jr., *J. Chem. Phys.* **83**, 6268-6274 (1985).
28. L. Adamowicz and R.J. Bartlett *Chem. Phys. Lett.* **129**, 159-164 (1986).
29. L. Adamowicz and R.J. Bartlett, *J. Chem. Phys.* **88**, 313-316 (1988).
30. L. Adamowicz, *J. Chem. Phys.* **91**, 7787-7790 (1989).
31. G.L. Gutsev and L. Adamowicz, *Chem. Phys. Lett.* **246**, 245-250 (1995).
32. N.A. Oyler and L. Adamowicz, *J. Phys. Chem.* **97**, 11122-11123 (1993).
33. N.A. Oyler and L. Adamowicz, *Chem. Phys. Lett.* **219**, 223-227 (1994).
34. G.H. Roehrig, N.A. Oyler, and L. Adamowicz, *Chem. Phys. Lett.* **225**, 265-272 (1994).
35. G.H. Roehrig, N.A. Oyler, and L. Adamowicz, *J. Phys. Chem.* **99**, 14285-14289 (1995).
36. G.L. Gutsev, A.L. Sobolewski, and L. Adamowicz, *Chem. Phys.* **196**, 1-11 (1995).
37. J. Smets, W.J. McCarthy, and L. Adamowicz, *J. Phys. Chem.* **100**, 14655-14660 (1996).
38. J. Smets, W.J. McCarthy, and L. Adamowicz, *Chem. Phys. Lett.* **256**, 360-369 (1996).
39. J. Smets, D.M.A. Smith, Y. Elkadi, and L. Adamowicz, *J. Phys. Chem. A* **101**, 9152-9156 (1997).
40. J. Smets, D.M.A. Smith, Y. Elkadi, and L. Adamowicz, *Pol. J. Chem.* **72**, 1615-1623 (1998).

41. D.M.A. Smith, J. Smets, Y. Elkadi, and L. Adamowicz, *J. Phys. Chem. A* **101**, 8123-8127 (1997).
42. Y. Elkadi and L. Adamowicz, *Chem. Phys. Lett.* **261**, 507-514 (1996).
43. D.M. Chipman, *J. Phys. Chem.* **83**, 1657-1662 (1979).
44. G.L. Gutsev, M. Nooijen, and R.J. Bartlett, *Chem. Phys. Lett.* **267**, 13-19 (1997).
45. G.L. Gutsev, M. Nooijen, and R.J. Bartlett, *Phys. Rev. A* **57**, 1646-1651 (1998).
46. G.L. Gutsev and R.J. Bartlett, *J. Chem. Phys.* **105**, 8785-8792 (1996).
47. M. Gutowski and P. Skurski, *J. Chem. Phys.* **107**, 2968-2973 (1997).
48. M. Gutowski and P. Skurski, *J. Phys. Chem. B* **101**, 9143-9146 (1997).
49. P. Skurski and M. Gutowski, *J. Chem. Phys.* **108**, 6303-6311 (1998).
50. M. Gutowski and P. Skurski, *Chem. Phys. Lett.* **300**, 331 (1999).
51. P. Skurski and M. Gutowski, *J. Chem. Phys.* **111**, 3004 (1999).
52. M. Gutowski, P. Skurski, and J. Simons, *J. Am. Chem. Soc.* **122**, 10159 (2000).
53. R. Barrios, P. Skurski, J. Rak, and M. Gutowski, *J. Chem. Phys.* **113**, 8961 (2000).
54. P. Skurski, M. Gutowski, and J. Simons, *J. Chem. Phys.* **114**, 7443 (2001).
55. J. Rak, P. Skurski, and M. Gutowski, *J. Chem. Phys.* **114**, 10673 (2001).
56. Y. Boutellier, C. Desfrancois, H. Abdoul-Carime, and J.P. Schermann, *J. Chem. Phys.* **105**, 6420-6425 (1996).
57. H. Abdoul-Carime and C. Desfrancois, *Eur. Phys. J. D* **2**, 149-156 (1998).
58. P. Skurski, M. Gutowski, and J. Simons, *J. Chem. Phys.* **110**, 274-280 (1999).
59. P. Skurski, M. Gutowski, and J. Simons, *J. Phys. Chem. A* **103**, 625-631 (1999).
60. A.H. Zimmerman and J.I. Brauman, *J. Chem. Phys.* **66**, 5823-5825 (1977).
61. R.L. Jackson, A.H. Zimmerman, and J.I. Brauman, *J. Chem. Phys.* **71**, 2088-2094 (1979).
62. R.L. Jackson, P.C. Hiberty, and J.I. Brauman, *J. Chem. Phys.* **74**, 3705-3712 (1981).
63. J. Marks, P.B. Comita, and J.I. Brauman, *J. Am. Chem. Soc.* **107**, 3718-3719 (1985).
64. J. Marks, D.M. Wetzel, P.B. Comita, and J.I. Brauman, *J. Chem. Phys.* **84**, 5284-5289 (1986).
65. D.M. Wetzel and J.I. Brauman, *J. Chem. Phys.* **90**, 68-73 (1989).
66. E.A. Brinkman, S. Berger, J. Marks, and J.I. Brauman, *J. Chem. Phys.* **99**, 7586-7594 (1993).
67. B.C. Romer and J.I. Brauman, *J. Am. Chem. Soc.* **119**, 2054-2055 (1997).
68. R.D. Mead, K.R. Lykke, W.C. Lineberger, J. Marks, and J.I. Brauman, *J. Chem. Phys.* **81**, 4883-4892 (1984).
69. T. Andersen, K.R. Lykke, D.M. Neumark, and W.C. Lineberger, *J. Chem. Phys.* **86**, 1858-1867 (1987).
70. K.R. Lykke, D.M. Neumark, T. Andersen, V.J. Trapa, and W.C. Lineberger, *J. Chem. Phys.* **87**, 6842-6853 (1987).
71. J. Marks, J.I. Brauman, R.D. Mead, K.R. Lykke, and W.C. Lineberger, *J. Chem. Phys.* **88**, 6785-6792 (1988).
72. A.S. Mullin, K.K. Murray, C.P. Schultz, D.M. Szaflarski, and W.C. Lineberger, *Chem. Phys.* **166**, 207-213 (1992).
73. A.S. Mullin, K.K. Murray, C.P. Schultz, and W.C. Lineberger, *J. Phys. Chem.* **97**, 10281-10286 (1993).
74. K. Yokoyama, G.W. Leach, J.B. Kim, and W.C. Lineberger, *J. Chem. Phys.* **105**, 10696-10705 (1996).
75. K. Yokoyama, G.W. Leach, J.B. Kim, W.C. Lineberger, A.I. Boldyrev, and M. Gutowski, *J. Chem. Phys.* **105**, 10706-10718 (1996).
76. C. Desfrancois, N. Khelifa, A. Lisfi, J.P. Schermann, J.G. Eaton, and K.H. Bowen, *J. Chem. Phys.* **95**, 7760-7762 (1991).
77. C. Desfrancois, B. Baillon, J.P. Schermann, S.T. Arnold, J.H. Hendricks, and K.H. Bowen, *Phys. Rev. Lett.* **72**, 48-51 (1994).
78. C. Desfrancois, H. Abdoul-Carime, C. Adjouri, N. Khelifa, and J.P. Schermann, *Europhys. Lett.* **26**, 25-30 (1994).

79. C. Desfrancois, H. Abdoul-Carime, N. Khelifa, J.P. Schermann, V. Brenner, and P. Millie, *J. Chem. Phys.* **102**, 4952-4964 (1995).
80. C. Desfrancois, H. Abdoul-Carime, C.P. Schulz, and J.P. Schermann, *Science* **269**, 1707-1709 (1995).
81. C. Desfrancois, *Phys. Rev. A* **51**, 3667-3675 (1995).
82. C. Desfrancois, H. Abdoul-Carime, and J.P. Schermann, *J. Chem. Phys.* **104**, 7792-7794 (1996).
83. R.N. Compton, H.S. Carman, Jr., C. Desfrancois, H. Abdoul-Carime, J.P. Schermann, J.H. Hendricks, S.A. Lyapustina, and K.H. Bowen, *J. Chem. Phys.* **105**, 3472-3478 (1996).
84. C. Desfrancois, H. Abdoul-Carime, and J.P. Schermann, *Int. J. Mod. Phys. B* **10**, 1339-1395 (1996).
85. H. Abdoul-Carime, A. Wakisaka, Y. Bouteiller, C. Desfrancois, and J.P. Schermann, *Z. Phys. D* **40**, 55-61 (1997).
86. H. Abdoul-Carime, W. Wakisaka, J. Flugge, H. Takeo, V. Periquet, J.P. Schermann, and C. Desfrancois, *J. Chem. Soc. Faraday Trans.* **93**, 4289-4293 (1997).
87. C. Desfrancois, V. Periquet, Y. Bouteiller, and J.P. Schermann, *J. Phys. Chem. A* **102**, 1274-1278 (1998).
88. C. Desfrancois, V. Periquet, C. Carles, J.P. Schermann, and L. Adamowicz, *Chem. Phys.* **239**, 475-483 (1998).
89. C.E.H. Dessent, C.G. Bailey, and M.A. Johnson, *J. Chem. Phys.* **103**, 2006-2015 (1995).
90. J.A.D. Stockdale, F.J. Davis, R.N. Compton, and C.E. Klots, *J. Chem. Phys.* **60**, 4279-4285 (1974).
91. R.N. Compton, P.W. Reinhardt, and C.D. Cooper, *J. Chem. Phys.*, **68**, 4360-4367 (1978).
92. J.V. Coe, G.H. Lee, J.G. Eaton, S.T. Arnold, H.W. Sarkas, and K.H. Bowen, Jr., *J. Chem. Phys.* **92**, 3980-3982 (1990).
93. J. H. Hendricks, H.L. de Clercq, S.A. Lyapustina, C.A. Fancher, T.P. Lippa, J.M. Collins, S.T. Arnold, G.H. Lee, and K.H. Bowen, in *Proceedings of the Yamada Conference No. XLIII, May 1995, Structure and Dynamics of Clusters*, Universal Academy Press: Tokyo, 1995.
94. J. H. Hendricks, S.A. Lyapustina, H.L. de Clercq, J.T. Snodgrass, and K.H. Bowen, Jr., *J. Chem. Phys.* **104**, 7788-7791 (1996).
95. A.W. Castelman, Jr., and K.H. Bowen, Jr., *J. Phys. Chem.* **100**, 12911-12944 (1996).
96. J.H. Hendricks, H.L. de Clercq, S.A. Lyapustina, and K.H. Bowen, Jr., *J. Chem. Phys.* **107**, 2962-2967 (1997).
97. C.E.H. Dessent, C.G. Bailey, and M.A. Johnson, *J. Chem. Phys.* **103**, 2006-2015 (1995).
98. C.E.H. Dessent, J. Kim, and M.A. Johnson *J. Phys. Chem.* **100**, 12-14 (1996).
99. D. Serxner, C.E.H. Dessent, and M.A. Johnson, *J. Chem. Phys.* **105**, 7231-1234 (1996).
100. C.E.H. Dessent, J. Kim, and M.A. Johnson, *Acc. Chem. Res.* **31**, 527-534 (1998).
101. C.G. Bailey, C.E.H. Dessent, M.A. Johnson, and K.H. Bowen, Jr., *J. Chem. Phys.* **104**, 6976-6983 (1996).
102. This molecule also has a valence-bound anion in addition to the dipole-bound state we refer to here.
103. P. Skurski, M. Gutowski, and J. Simons, *Int. J. Quantum Chem.* **80**, 1024 (2000).
104. F. Wang and K. D. Jordan, *J. Chem. Phys.* **114**, 10717 (2001).
105. O. H. Crawford and W. R. Garrett, *J. Chem. Phys.* **66**, 4968 (1977). In this paper, the authors examine a rotating FFD model and determine how large must be to effect electron binding for various rotational constants (i.e., various moments of inertia).
106. J.V. Coe, G.H. Lee, J.G. Eaton, S.T. Arnold, H.W. Sarkas, and K.H. Bowen, Jr., *J. Chem. Phys.* **92**, 3980-3982 (1990);
107. L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (2nd Ed.), Pergamon Press, Oxford, England (1965).

108. This trial function was suggested by Prof. E. R. Davidson in August of 1998 in a personal communication to J. S. We are most appreciative for the thoughtful analysis given to this problem by Prof. Davidson.
109. K. D. Jordan and J. F. Liebman, *Chem. Phys. Lett.* **62**, 143 (1979).
110. M. Gutowski and P. Skurski, *Chem. Phys. Lett.* **303**, 65 (1999).
111. R. N. Compton, F. B. Dunning, and P. Nordlander, *Chem. Phys. Lett.* **253**, 8 (1996).
112. C. Desfrancois, V. Periquet, S. A. Lyapustina, T. P. Lippa, W. Robinson, K. H. Bowen, H. Nonaka, and R. N. Compton, *J. Chem. Phys.* **111**, 4569 (1999).
113. See, for example, G. Herzberg, *Faraday Discuss. Chem. Soc.* **71**, 165-173 (1981) and G.I. Gellene, D.A. Cleary, and R. Porter, *J. Chem. Phys.* **77**, 3471-3477 (1982).
114. For example, see: J. Kalcher, P. Rosmus, and M. Quack, *Can. J. Phys.* **62**, 1323-1327 (1984); H. Cardy, C. Larrieu, and A. Dargelos, *Chem. Phys. Lett.* **131**, 507-512 (1986); D. Cremer and E. Kraka, *J. Phys. Chem.* **90**, 33-40 (1986); J.V. Ortiz, *J. Chem. Phys.* **87**, 3557-3562 (1987); J. V. Ortiz, *J. Phys. Chem.*, **94** 4762-4763 (1990); K.H. Bowen and J.G. Eaton, The Structure of Small Molecules and Ions, R. Naaman and Z. Vager, Eds., Plenum Press: New York, 1987, p 147; S.T. Arnold, J.G. Eaton, D. Patel-Misra, H.W. Sarkas, and K.H. Bowen, Ion and Cluster Ion Spectroscopy and Structure, J.P. Maier, Ed., Elsevier: Amsterdam, 1989; M. Gutowski, H. Taylor, R. Hernandez and J. Simons, *J. Phys. Chem.* **92**, 6179 (1988); J. Simons and M. Gutowski, *Chem. Rev.* **91**, 669 (1991).
115. P. Skurski, M. Gutowski and J. Simons, *Int. J. Quant. Chem.*, **76**, 197 (2000).
116. C. Sarasola, J. E. Fowler, and J. M. Ugalde, *J. Chem. Phys.* **110**, 11717 (1999); C. Sarasola, J. E. Fowler, J., M. Elorza, and J. M. Ugalde, *Chem. Phys. Lett.* **337**, 355 (2001).
117. P. Skurski and J. Simons, *J. Chem. Phys.* **112**, 6563 (2000).
118. L.-S. Wang and X-B. Wang, *J. Phys. Chem.* **104**, 1978 (2000).
119. J. Simons, P. Skurski, and R. Barrios, *J. Am. Chem. Soc.* **122**, 11893 (2000).
120. P. Skurski, M. Gutowski, and J. Simons, *Chem. Phys. Lett.* **322**, 175 (2000).
121. T. Sommerfeld, *J. Phys. Chem.*, **A104**, 8806 (2000)
122. M. Gutowski, A. I. Boldyrev, J. V. Ortiz, and J. Simons, *J. Am. Chem. Soc.*, **116**, 9262-9268 (1994).
123. P. Weis, O. Hampe, S. Gilb, and M. M. Kappes, *Chem. Phys. Lett.* **321**, 426 (2000).
124. A. I. Boldyrev and J. Simons, *J. Chem. Phys.* **97**, 2826 (1992).
125. M. K. Scheller, R. N. Compton, and L. S. Cederbaum, *Science*, **270** 1160-1166 (1995).
126. H-G. Weikert, L. S. Cederbaum, F. Tarantelli, and A. I. Boldyrev, *Z. Phys. D* **18**, 229 (1991);
127. H-G. Weikert and L. S. Cederbaum, *J. Chem. Phys.* **99**, 8877 (1993).