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# Finding Valence Antibonding Levels while Avoiding Rydberg, Pseudo-continuum, and Dipole-Bound Orbitals

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**ABSTRACT:** Electronic structure methods are now widely used to assist in the interpretation of many varieties of experimental data. The energies and physical characteristics (e.g., sizes, shapes, and spatial localization) of valence antibonding  $\pi^*$  and  $\sigma^*$  orbitals play key roles in a variety of chemical processes including photochemical reactions and electron attachment reductions and are used in Woodward–Hoffmann-type analyses to probe reaction energy barriers and energy surface intersections leading to internal conversion or intersystem crossings. One's ability to properly populate such valence antibonding orbitals within electronic structure calculations is often hindered by the presence of other molecular orbitals having similar energies. These intruding orbitals can be of Rydberg, pseudo-continuum, or dipole-bound character-



istic. This article shows how, within the most widely available electronic structure codes, one can avoid the pitfalls presented by these intruding orbitals to properly populate a valence  $\pi^*$  or  $\sigma^*$  orbital and how to subsequently use that orbital in a calculation that includes electron correlation effects and thereby offers the possibility of chemically useful precision. Special emphasis is given to cases in which the electronic state is metastable.

# 1. INTRODUCTION

This paper is directed primarily at researchers who make use of electronic structure theory to guide their experimental or theoretical studies but who are not experts in the field. For this reason, much of the pedagogical material treated early will likely be of less interest to scholars who specialize in this field, but we hope that even these individuals will derive benefit from the material appearing later that presents new ideas and results. In 1991, one of us published another pedagogical paper<sup>1</sup> aimed at the same audience, but the present paper deals with a specific topic that we believe requires further emphasis-how to focus on desired valence  $\pi^*$  and  $\sigma^*$  antibonding levels and avoid having the computer code populate unwanted Rydberg, pseudo-continuum (PC), or dipole-bound levels whose origins are explained later. Achieving this goal is especially challenging when the valence antibonding level is metastable with respect to electron detachment as it then exists within a cluster of PC levels having similar energies and is difficult to identify.

The purpose of this work is to provide a reliable path by which the researcher can direct the electronic structure program to occupy the valence antibonding orbital the researcher has in mind. For pedagogical reasons, such a path is described for treating states in which a valence  $\pi^*$  orbital of an olefin is populated either by electron addition (i.e., in a reductive process) or by electron promotion (e.g., by excitation from a lower energy orbital), but this path is applicable to a wide range of other cases such as populating  $\sigma^*$  orbitals in hydrocarbons or in disulfide bonds,  $\pi^*$  orbitals in DNA bases,  $\pi^*$  orbitals delocalized over OCN units in polypeptides,  $\pi^*$ orbitals in poly-aromatic compounds, and so forth.

When carrying out electronic structure calculations using a method based on one dominant electronic configuration [e.g., Hartree–Fock (HF) or density functional theory (DFT)], one has one set of spin–orbitals (i.e., an orbital and either an  $\alpha$  or a  $\beta$  spin function) that are occupied by an electron and a complementary set of spin–orbitals that contain no electrons. It is common to refer to these as occupied and virtual spin–orbitals, respectively. Even when using a method that expresses the electronic wave function in terms of a superposition of many configurations [e.g., Møller–Plesset perturbation theory (MPPT), configuration interaction (CI), multi-configuration self-consistent field theory (MCSCF), and coupled-cluster theory (CC)], it is possible and often true that one configuration can be dominant. In such cases, one can speak

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of the spin-orbitals appearing in the dominant configuration as "occupied" (actually strongly but not totally occupied) and the other spin-orbitals as "virtual" (even though they may appear in some of the non-dominant electronic configurations).

In this manuscript, we will employ a simple but illustrative example involving an olefin  $R_2C = CR'_2$  in its ground electronic state with various substituents R and R' and we will focus on the valence-occupied  $\pi$  and virtual  $\pi^*$  orbitals involving its two central C atoms. Moreover, we will employ primarily a HFlevel treatment when discussing the orbitals involved because doing so provides a clear demarcation between occupied and virtual orbitals. However, the issues and lessons thus treated could instead be illustrated using DFT-level orbitals. As noted earlier, although the quantitative results we show (e.g., orbital energies and orbital plots) pertain to the olefin examples, the issues we raise and attempt to clarify apply to a wide variety of situations in which one is faced with how to describe states that populate valence antibonding  $\pi^*$  and  $\sigma^*$  virtual orbitals belonging to other functional units appearing in small and large molecules.

Note that there are two distinct types of antibonding  $\pi^*$  orbitals that we are discussing here:  $\pi^*$  orbitals of a molecule populated in a reductive electron attachment reaction and  $\pi^*$  orbitals that are occupied when that molecule is promoted, for example, to a  $\pi\pi^*$  or  $n\pi^*$  excited state. These  $\pi^*$  orbitals differ substantially and need to be treated differently. The  $\pi^*$  orbital of an electron-attached state experiences Coulomb and exchange interactions with two electrons residing in the bonding  $\pi$  orbital, while the  $\pi^*$  orbital in the  $\pi\pi^*$  excited state experiences an interaction with only one such electron. As a result, the former  $\pi^*$  orbital has a smaller electron binding energy (and may even be unbound) and thus has a larger radial extent, while the latter has a larger binding energy and is more radially compact.

In 2020, Krylov provided a wonderful perspective article<sup>2</sup> in which she explained in more detail how the  $\pi^*$  electronattached states and  $\pi^*$  excited states can be obtained using more sophisticated methods than through the approach utilized here. Moreover, she does a good job of illustrating how the two types of  $\pi^*$  orbitals occupied in these states differ in size and electron binding strengths. Other workers<sup>3-8</sup> have described how these and alternative  $\pi^*$  orbitals (e.g., localized  $\pi^*$  orbitals and  $\pi^*$  orbitals used for inter-fragment interaction energy calculations) can be extracted from electronic structure calculations. We raise the point to emphasize that there is not one type of olefin  $\pi^*$  orbital; various utilizations of the concept of the  $\pi^*$  orbital require various quantitative definitions. In this paper, we focus on the two types that relate to electron addition and electron excitation. Moreover, we offer guidance for how to handle situations in which the resultant  $\pi^*$ populated states are metastable with respect to electron loss using tools that are present in most electronic structure codes.

As related to the olefin case, the issues we address here include

a How does one identify (i.e., obtain in an electronic structure calculation) the electron-attached state in which a valence antibonding molecular orbital (MO) is populated when this olefin undergoes reductive electron attachment? It is tempting to assume that this orbital will be the lowest energy unoccupied molecular orbital (LUMO) of the parent olefin, but often that is not the case. If the parent olefin contains positively charged groups, it can possess lower energy Rydberg orbitals localized on these groups. If the olefin is very polar, it might have a so-called dipole-bound orbital. Plus, when large diffuse atomic orbital basis sets are used, low-energy PC orbitals (i.e., orbitals relating to the parent molecule with the extra electron in a very diffuse orbital essentially detached from the parent) often arise. One needs to know how to guide the calculation toward populating the desired valence antibonding orbital rather than one of the Rydberg, PC, or dipole-bound orbitals.

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b How does one identify the state in which an electron has been excited from a lower-energy-occupied orbital into a valence  $\pi^*$  orbital as would be appropriate for describing the singlet or triplet  $\pi\pi^*$  excited state of the olefin? Again, there can be orbitals having energies below that of the valence  $\pi^*$  orbital and one needs to guide the calculation toward occupying the proper orbital.

In both of the above cases, it is important to realize that the attached or  $\pi\pi^*$  excited state might lie above the energy of the parent or above the parent's ionization threshold, respectively, and thus be metastable with respect to electron loss. In such situations, it becomes especially difficult to treat the state of interest because the valence characteristic of its wave function becomes intertwined with components of the wave function in which the PC orbitals are occupied. This paper describes how to handle such metastable-state situations using tools that are present in most electronic structure codes.

- c The olefin's functional groups might generate a molecule that is sufficiently polar to allow the molecule to possess a so-called dipole-bound anionic state,<sup>9,10</sup> and this is most likely to occur when one is using a basis set containing very diffuse functions. For example,  $(NC)_2C = CH_2$  has a dipole moment of 5.13 Debyes and can bind an electron on its partially positive end to form  $[(NC)_2C=CH_2]^-$  as a dipole-bound anion. In such cases, the LUMO of the parent olefin is likely to be this dipole-bound orbital and to have a negative orbital energy, whereas the  $\pi^*$  orbital one is searching for can have a HF orbital energy far above the energy of the LUMO. In these cases, the dipole-bound orbitals are a nuisance, and one needs to know how to avoid them so that one can focus on the desired  $\pi^*$  orbital either if one wants to study the addition of an electron to the  $\pi^*$ orbital or formation of a  $\pi\pi^*$  excited state.
- d The molecule containing the olefin unit might contain one or more positively charged sites such as a protonated side chain of a peptide. In such cases, the LUMO (and probably more) will likely be the so-called Rydberg-like orbitals centered on the positive site and having an electron binding energy in the 1–4 eV range. As was the case for the dipole-bound orbital, one needs to be able to avoid populating such orbitals so that one can populate the desired  $\pi^*$  orbital.
- e Alternatively, as for  $(NC)_2C=C(CN)_2$ , the substituents can provide sufficient electron-stabilizing influence to render the olefin's  $\pi^*$  orbital bound (i.e., to have a negative HF orbital energy). In such a case, the neutral's LUMO can offer a good description of the  $\pi^*$  orbital one is trying to find if one is searching for the orbital occupied in the anion. Although this case is more straightforward to treat, it is discussed as a means of

introducing a technique that one can use when the desired  $\pi^*$  orbital has a positive HF orbital energy. In this technique, one introduces an artificial electron-stabilizing potential to the olefin's two C atoms. This potential acts to differentially stabilize orbitals such as the desired  $\pi^*$  orbital that possess high amplitudes near these C atoms. Later in this manuscript, we will demonstrate the use of this technique as a powerful method for properly identifying and characterizing (by energy) the anion's  $\pi^*$  orbital. However, we will also demonstrate a pitfall that can plague such an electron stabilization method and offer ideas about how to avoid such problems.

Finally, it should be emphasized that although much of the discussion presented here is focused on orbitals, especially virtual HF orbitals, we do not want to suggest that once an appropriate antibonding orbital has been found the work is done. It is well known that orbital energies alone do not provide very accurate estimates for the energy involved in attaching (i.e., for virtual orbitals), detaching (for occupied orbitals), or exciting an electron. We assume that the researcher will subsequently employ a method that treats electron correlation (e.g., MPPT, CI, MCSCF, CC, or DFT or a method that computes the electron attachment or excitation energy directly) to achieve an accurate value for the electron attachment, detachment, or excitation energy. However, the first step in any such plan is to properly identify the proper antibonding orbital and guide the computer program to populate this orbital, and how to do so is a primary focus of this paper.

# 2. METHODS

The equilibrium geometry structures of the neutral ethylene (ethene,  $H_2C=CH_2$ ), dicyanoethylene (1,1-dicyanoethene, (CN)<sub>2</sub>C=CH<sub>2</sub>), and tetracyanoethylene (TCNE, (NC)<sub>2</sub>C=C(CN)<sub>2</sub>) were obtained by applying the second-order Møller–Plesset perturbation method (MP2)<sup>11–13</sup> using a 6-31++G(d,p)<sup>14–16</sup> basis set for all atoms. In all cases, the harmonic vibrational frequencies characterizing the stationary-point structures were evaluated at the same level of theory to assure that they correspond to true minima on the potential energy surface.

The HF orbital energies of the highest occupied molecular orbital (HOMO) and of the LUMO + n (n = 0-7) were obtained from calculations performed with the 6-31++G(d,p) basis set. Unless otherwise specified, this same basis set was used for all other calculations.

The LUMO of the neutral  $(NC)_2C=CH_2$  was obtained by using the 6-31++G(d,p) basis set supplemented with a 4(sp)2d set of diffuse functions centered on the carbon atom of the =CH<sub>2</sub> group (since this is the centroid of the positive end of the dipole). The extra diffuse functions, which were added to describe the very diffuse dipole-bound orbital that is expected to arise for this species, share exponent values and we used even-tempered<sup>17</sup> four-term sp and twoterm *d* basis sets. The geometric progression ratio was equal to 3.2,<sup>18</sup> and, for each symmetry, we started the exponents of the extra diffuse functions from the lowest exponent of the same symmetry included in the 6-31++G(d,p) basis set designed for carbon. We examined the lowest eigenvalue of the atomic orbital overlap matrix to determine that near-linear dependency was not a problem.

When carrying out calculations in which a stabilizing electronic potential is used to render electronically metastable states stable, either of two routes were used. In one, excess charges are added to some of the atomic nuclei to produce a potential that is stabilizing in these regions of space. In the second, a dielectric continuum solvation potential is added to generate the stabilization. In the latter, the electronic energies of the states for a range of dielectric constant ( $\epsilon$ )

values for which the anion is stable were obtained by employing the polarized continuum solvation model  $(PCM)^{19-21}$  within a selfconsistent reaction field treatment, as implemented in the GAUSSIAN16 (Rev. B.01) package (the default options for PCM and dielectric constants spanning the 2–78 range were used).

In these PCM studies, the Koopmans' theorem<sup>22</sup> electron affinities (EA<sup>KT</sup>) were obtained from the energy of the singly occupied molecular (taken with the opposite sign) of the anion stabilized by the solvent effects approximated by the PCM. The CC-level EAs labeled EA<sup>CC</sup> were determined by subtracting the energy of the anion from that of the neutral (both stabilized by the solvent effects approximated by the PCM in the dielectric stabilization studies) calculated using the CC method with single, double, and non-iterative triple excitations (CCSD(T))<sup>23–26</sup> and either the 6-31++G(d,p) or the aug-cc-pVTZ<sup>27,28</sup> valence basis set.

All calculations were performed with the GAUSSIAN16 (Rev.B.01) package.<sup>29</sup>

# 3. RESULTS AND DISCUSSION

3.1. Electron-Attached State of Ethylene with an Electron in the Valence  $\pi^*$  Orbital. In Figure 1, we show



**Figure 1.** Plots of the HOMO and eight virtual orbitals of ethylene. In each case, ca. 88% of the electron density is included within the outermost contour of the plot, and the orientation and physical size of the underlying molecular framework is essentially the same in all plots.

plots of HF orbitals and the HF orbital energies of the occupied bonding  $\pi$  orbital and of several low-energy virtual orbitals for the neutral ethylene molecule obtained using the atomic orbital basis set described in the Methods section. All of the plots show orbitals that contain within their outermost contours ca. 88% of the electron density, which allows one to accurately judge their radial sizes. Notice that the HOMO is quite small, which reflects its strong electron binding strength of ca. 10 eV. For the LUMO + *n* orbitals, of course, there is no electron occupying them in the neutral, but we still plot them

as though an electron was present, and their radial sizes are related to and limited by the radial extent of the atomic orbital basis set rather than to their HF energies.

Looking at these orbital plots, it is relatively straightforward, based on its symmetry, to conclude that the orbital-labeled LUMO + 4 is a good candidate for the  $\pi^*$  orbital. The high symmetry of this molecule and the fact that not many lowenergy virtual orbitals are shown in Figure 1 seem to make this identification straightforward. However, this identification is actually not rigorously correct, although it is a reasonable approximation, and later, we will explain how to achieve a more accurate description of the desired  $\pi^*$  orbital.

Next, it is important to explain what the LUMO through LUMO + 3 (and some of the higher LUMO + K; K > 4) orbitals are because it is their presence that complicates finding a more proper  $\pi^*$  orbital in many cases. They are approximations to orbitals describing an electron-attached state in which the excess electron is contained in a continuum orbital (i.e., an orbital not bound to the valence framework of the olefin but with the extra electron unbound and scattering off of the neutral olefin). Because our HF calculation was carried out with a finite basis of square-integrable atomic basis functions, it does not produce true continuum functions but only approximate descriptions of them. For each such PC function, the kinetic energy of the unbound electron is given (approximately) by the HF energy of that orbital. For example, the LUMO orbital approximates an electron having a kinetic energy of ca. 1.35 eV, as reflected in this (positive) value for its HF orbital energy; the other LUMO + K(K > 4) PC orbitals approximate free electrons of higher kinetic energy.

One might ask why it is not possible to eliminate these PC orbitals by eliminating the diffuse atomic basis functions used in the calculation, thus making the LUMO + 4 orbital the LUMO. Indeed, several years ago, Staley<sup>30</sup> and Gallup<sup>31</sup> showed that when using STO-3G or 6-31G basis sets, which contain no diffuse functions, experimentally measured electron attachment energies  $E_{\mathrm{expt}}$  for several metastable  $\pi^*$ - and  $\sigma^*$ attached states of saturated and unsaturated hydrocarbons produced a linear-fit relationship with the Koopmans theorem (KT) LUMO-orbital estimate. However, such studies do not exist for many of the species one is likely to encounter, and, in our opinion, eliminating diffuse basis functions is not wise because these functions are needed for accurately describing the large-r "tails" of the olefin's occupied orbitals; without them, the description of the neutral's occupied orbitals would suffer. The fact is that adding diffuse basis functions is essential for the latter reason even though it causes the calculation to also generate low-energy HF virtual orbitals of PC characteristic, and thus, one needs to know how to avoid mistakenly identifying them as the desired  $\pi^*$  orbital.

As noted above, in Figure 1, it is relatively easy to choose LUMO + 4 as a candidate for the  $\pi^*$  orbital because of the high symmetry and small size of the ethylene molecule. However, for an olefinic unit embedded within a large molecular framework, there likely would be far more PC orbitals, other low-energy antibonding orbitals, and no point group symmetry, as a result of which finding the desired  $\pi^*$  orbital would be more challenging. The more diffuse basis functions one uses (e.g., to enhance the description of the occupied orbitals' radial tails), the more PC orbitals will have energies below that of the putative  $\pi^*$  orbital. Moreover, if the energies of one or more PC orbitals having the same symmetry as that of LUMO + 4 turns out to be close to that of the  $\pi^*$ 

orbital, the situation becomes even more complicated. For example, if there had been substituents on the ethylene that reduce the molecular symmetry, the LUMO + 4 orbital could mix with the other virtual orbitals, especially with those having similar energies. This would cause more than one of the plots of the virtual orbitals near in energy to LUMO + 4 to display significant  $\pi^*$  characteristic which, in turn, would make it difficult to impossible to decide which orbital to "guess" to be the  $\pi^*$  orbital. It is precisely this mixing or coupling of the valence-type  $\pi^*$  orbital (e.g., LUMO + 4) with PC orbitals of the same symmetry and of similar HF energies that produces the finite lifetime of the  $\pi^*$ -attached olefin state. Later in this paper, we will say more about how such lifetimes can be estimated.

Notice that above and for the remainder of this paper, we use HF orbitals and orbital energies to guide our orbital search. We do not employ virtual orbitals obtained from a DFT calculation because the energies of such virtual orbitals have not been shown,<sup>32</sup> except in improvements<sup>33</sup> to DFT, to have as direct and reliable a connection to the EAs of the neutral molecules as do the HF virtual orbitals. In contrast, HF virtual orbitals are known, through Koopmans' theorem<sup>22</sup> (KT), to provide a rigorous, albeit approximate, estimate to EAs. We know that as the development of DFT theory progresses, this situation will be remedied to an extent that the DFT methods appearing in most commonly available software will produce virtual orbital energies that can be used instead of HF orbital energies. However, at this time and for this pedagogical article, we prefer to make use of HF orbitals and orbital energy data. Others may prefer to use DFT orbitals and their energies, and we note that Baerends<sup>34</sup> and Hoffmann<sup>35</sup> have shown how DFT orbitals can be used to gain qualitatively useful insights into a wide range of chemical issues as long as one is careful to recognize the systematic errors their orbital energies tend to make especially in predicting EAs. In ref 34, the author explains the differences between HF and DFT orbitals and discusses some of the trends in occupied and virtual orbital energies, and in ref 35, the authors discuss the systematic differences between the HF and DFT virtual (and occupied) orbital energies and emphasize how the shapes and sizes of the two classes of orbital are quite similar. Finally, we also note that in ref 8, it has been shown how advances in DFT can be made to construct valence antibonding orbitals appropriate for use in describing excited states.

One might assume that simply by using a description of the electron-attached state's wave function that goes beyond the single-configuration level, one can avoid the problem of PC orbitals, but this is not correct. In most correlated wave function-based approaches (e.g., CI, MPPT, MCSCF, CC, and DFT), one must specify the occupation of the spin-orbitals that appear in the presumed dominant electronic configuration. For the ethylene example, if one specifies that the LUMO (or LUMO + 1, LUMO + 2, or LUMO + 3) is occupied, one will generate a correlated (i.e., meaning described beyond the single-configuration level) energy for the neutral olefin with the extra electron in a PC orbital, which is not what one wants. Even if one specifies that the LUMO + 4 is to be singly occupied, problems can arise if the method used to determine the correlation energy allows for the virtual orbitals to be "optimized" (i.e., to undergo a unitary linear transformation) during its convergence process. Any optimization that aims to lower the total electronic energy, which is what variational-based methods do, could allow the singly

occupied orbital to evolve from the LUMO + 4 (at the first step of the optimization process) into a lower energy orbital (even the LUMO) as the energy optimization proceeds. This so-called variational collapse would again generate an energy appropriate to the parent olefin with the extra electron in a PC orbital and is most likely to occur when one is using a basis set

with diffuse functions that thus give rise to PC orbitals. Difficulties also arise if one chooses to employ methods that directly calculate the EA rather than by calculating separate energies of the parent and electron-attached species and subtracting these two energies. For example, using equationsof-motion CC (EOM-CC) methods,36,37 one has to specify how many eigenvalues (or within what energy range to look for such eigenvalues) of a matrix to extract the desired EA or excitation energy value. The matrices that arise in such theories are correlated analogs of the Fock matrix one uses in HF calculations where, as detailed earlier, one has to be careful to choose the proper virtual orbital in searching for the  $\pi^*$  orbital. Many of the EOM-CC eigenvalues can correspond to attaching the extra electron to a PC orbital or exciting an electron into such an orbital, so again one has to be able to identify the eigenvalue that describes attachment to or excitation into the desired antibonding orbital.

Hopefully, this discussion has made it clear that one needs to have a better route for identifying the  $\pi^*$  orbital and for computing the electron-attached or electron-excited state's energy when this orbital is occupied, and we will describe two such methods later in this paper that are straightforward to implement using widely available computer codes.

**3.2. What about Finding the**  $\pi^*$  **Orbital of the Singlet or Triplet**  $\pi\pi^*$  **Excited State of the Olefin?** To obtain a  $\pi^*$ orbital appropriate for states in which an electron has been promoted into this orbital, one could carry out a timedependent DFT (TD-DFT) or CI using singly excited electronic configuration (CIS) calculation for the parent olefin, specifying either triplet or singlet symmetry, and searching for excited states of  $\pi\pi^*$  or  $\pi\pi^*$  characteristic (by plotting the orbitals into which the electron has been excited). The  $\pi^*$ orbital one would find for a  $\pi\pi^*$  excited state would not be identical to that one would find for an  $\pi\pi^*$  excited state; the former would experience interactions with one occupied  $\pi$  $\sigma\pi\iota\nu$ -orbital (as well as with electrons in the other occupied orbitals), while the latter would have interactions with two occupied  $\pi$  spin-orbitals.

To illustrate the difference between the  $\pi^*$  orbitals in the  $\pi\pi^*$  excited state and in the electron-attached state, it suffices to recall the analytical expression for the energies of these two orbitals. The latter's HF orbital energy (assuming that one can provide a good approximation to that  $\pi^*$  orbital  $\phi_{\pi^*anion}$ ) is given by

$$\varepsilon_{\pi^* \text{anion}} = \left\langle \phi_{\pi^* \text{anion}} \right| - \frac{1}{2} \nabla^2 - \sum_a \frac{Z_a}{|r - R_a|} \left| \phi_{\pi^* \text{anion}} \right\rangle$$
$$+ \sum_{j=1}^N \left[ \left\langle \phi_{\pi^* \text{anion}}(r) \phi_j(r') \right| \frac{1}{|r - r'|} \phi_{\pi^* \text{anion}}(r) \phi_j(r') \right\rangle - \left\langle \phi_{\pi^* \text{anion}}(r) \phi_j(r') \left| \frac{1}{|r - r'|} \right| \phi_j(r) \phi_{\pi^* \text{anion}}(r') \right\rangle \right]$$
(1)

which is the kinetic energy plus the sum over all atomic nuclei (labeled *a*) of the Coulombic attractions to those nuclei plus the sum of the Coulomb minus exchange interactions with all *N* of the neutral olefin's occupied spin—orbitals (labeled  $\phi_j$ ). In contrast, the HF orbital energy of the triplet  $\pi\pi^*$  state's  $\pi^*$  orbital is given by

$$\varepsilon_{\pi^{*}\text{triplet}} = \left\langle \phi_{\pi^{*}\text{triplet}} \middle| -\frac{1}{2} \nabla^{2} - \sum_{a} \frac{Z_{a}}{|\mathbf{r} - R_{a}|} \middle| \phi_{\pi^{*}\text{triplet}} \right\rangle$$

$$+ \sum_{j=1}^{N-1} \left[ \left\langle \langle \phi_{\pi^{*}\text{triplet}}(r)\phi_{j}(r') \middle| \frac{1}{|\mathbf{r} - r'|} \phi_{\pi^{*}\text{triplet}}(r) \right.$$

$$\phi_{j}(r') \left\rangle - \left\langle \phi_{\pi^{*}\text{triplet}}(r)\phi_{j}(r') \middle| \frac{1}{|\mathbf{r} - r'|} \middle| \phi_{j}(r) \right.$$

$$\phi_{\pi^{*}\text{triplet}}(r') \left\rangle \right]$$

$$(2)$$

The most important difference between these two orbital energy expressions is that in eq 2, the sum of Coulomb minus exchange interactions contains only N-1 terms, while in eq 1, it contains N terms. The Coulomb and exchange integrals missing in eq 2 that appear in eq 1 involve  $\phi_j$  being the occupied  $\pi$  spin-orbital from which the electron was promoted to form the triplet  $\pi\pi^*$  state. The electron-attached state's  $\pi^*$  orbital experiences a Coulomb minus exchange interaction with this occupied  $\pi$  spin-orbital, but the  $\pi\pi^*$ state's  $\pi^*$  orbital does not. This is why the two  $\pi^*$  orbitals are not identical and why they are different from the  $\pi^*$  orbital of an  $n\pi^*$  state.

As an alternative to performing a TD-DFT or CIS calculation on the parent olefin when studying the  $\pi\pi^*$  state, one could carry out a HF calculation in which one has removed one of the two electrons occupying the bonding  $\pi$  orbital (e.g., remove the  $\beta$ -spin electron from the  $\pi$  orbital, thus leaving only the  $\alpha$ -spin electron). One could then examine this species' virtual HF  $\alpha$ -spin—orbitals and try to find a  $\pi^*$  orbital that could be used to form the triplet  $\pi\pi^*$  state of the parent. This is a reasonable route for finding a decent approximation to the triplet state's  $\pi^*$  orbital, but again, this orbital is different from the  $\pi^*$  orbital of the electron-attached species and would not be appropriate to use in that case. These differences are reflected in the radial extents of the neutral and cation  $\pi^*$  orbitals as shown in Figure 2 along with their HF orbital energies.

The cation's  $\alpha$ -spin-orbital (top left) has a very large negative HF orbital energy as this is the Koopmans' theorem estimate of the energy required to remove an electron from it to form the dication. The  $\alpha$ -spin-orbital LUMO (top right) is the one that would be used to describe the  $\pi^*$  orbital in a triplet  $\pi\pi^*$  state since the cation has its unpaired electron in an  $\alpha$  spin-orbital. The  $\beta$  spin-orbital LUMO (bottom left) is of  $\pi$  bonding characteristic and is this calculation's estimate of the orbital into which an electron would go to reform the ground state of the neutral.

Finally, the orbital shown on the bottom right of Figure 2 is the LUMO + 4 of the neutral olefin. Notice that this LUMO + 4 orbital is more diffuse and has a positive orbital energy (i.e., is unbound), while the excited state's  $\alpha$ -spin  $\pi^*$  (top right) orbital is more contracted and has a negative orbital energy (meaning this state lies below the ionization threshold). Even if



**Figure 2.** For the ethylene cation, the singly occupied (bonding  $\pi$ )  $\alpha$  spin-orbital (top left); lowest unoccupied  $\alpha$  spin-orbital ( $\pi^*$ ) (top right); lowest unoccupied  $\beta$  spin-orbital (bonding  $\pi$ ) (bottom left); and  $\pi^*$  of the neutral ethylene as in Figure 1 (bottom right). In all cases, ca. 88% of the electron density resides within the outer contour.

one were to consider the energy of the singlet  $\pi\pi^*$  state, whose zeroth-order wave function requires two Slater determinants rather than one as for the triplet state, the situation would remain the same; its  $\pi^*$  is more like that of the triplet  $\pi\pi^*$  state and quite different from that of the anion.

If one were to try to find a  $\pi^*$  orbital to use in describing a  $\pi\pi^*$  excited state using TD-DFT, CIS, or more sophisticated direct calculation methods, one might encounter a problem that is similar to that arising in the search for  $\pi^*$  orbitals to use in treating the electron-attached species. In particular, one might find that the  $\pi\pi^*$  state is predicted to have an energy higher than that of the parent species with one electron removed. That is, in the TD-DFT or CIS calculation, the  $\pi\pi^*$ excitation energy might exceed the ionization potential (IP) of the parent olefin. Although this may be unlikely to occur for a neutral parent olefin, if the parent has a negatively charged group somewhere else, the  $\pi\pi^*$  excitation energy of the olefinic unit could exceed the electron detachment energy of this negative group. This occurs, for example, in the  $H_2C-CN^$ anion<sup>38</sup> in which the excess electron is bound to a valence orbital in the ground state by only ca. 1.5 eV and in a dipolebound excited state by ca. 66  $\text{cm}^{-1}$ . Hence, one is faced with a  $\pi\pi^*$  excited state that lies within the continuum consisting of the parent molecule plus an electron in a continuum orbital. In such cases, one will be faced with using one of the approaches discussed below to more accurately treat metastable states such as this  $\pi\pi^*$  state.

**3.3. Two Devices for Finding the Antibonding**  $\pi^*$ **Orbital for Metastable Electron-Attached or Excited States.** There exist a variety of theoretical methods<sup>39–56</sup> that involve using complex variable mathematics within the electronic structure code for treating the energies and lifetimes of metastable electronic states. Some of these methods are included in certain of the widely available computational chemistry computer programs, but others reside in codes used less widely by the broader chemistry community and remain cutting-edge developments used primarily by the scientists who are developing them. We think it wise and entirely appropriate for a researcher to explore learning how to use such tools because they are likely to become more prevalent in future years, but here we are offering two approaches that are less mathematically complicated and that most workers can implement using most computational chemistry software and a little independent effort.

Before explaining how the first such method operates, let us briefly consider what happens when we carry out a HF calculation on the  $(NC)_2C=C(CN)_2$  TCNE molecule using a basis set similar to that used for ethylene as detailed in the Methods section. In this case, the LUMO turns out to be bound (by 1.98 eV) and, as shown in Figure 3, is clearly of  $\pi^*$ 



Figure 3. LUMO of tetracyano-ethylene obtained using the atomic orbital basis specified in the Methods section; 88% of the electron density is included within the outermost contour.

characteristic. In this case, it is no surprise that the electron withdrawing and delocalizing influences of the CN substituents have generated a potential that has stabilized the olefin's  $\pi^*$  orbital to an extent that renders it bound (i.e., having a negative HF orbital energy).

While this result probably is not surprising, we use it to introduce the first computational technique that has proven useful for finding  $\pi^*$  orbitals corresponding to metastable electron-attached states such as the ethylene molecular anion discussed earlier. In the so-called charge stabilization method pioneered by Nestmann and Peyerimhoff,<sup>57</sup> one adds to the nuclear charges  $\{Z_{n}\}$  of those nuclei over which one expects the desired  $\pi^*$  orbital to predominantly be localized a "small" amount  $\delta q$  (usually <1 in magnitude). For the ethylene case, one would set the charges of the two C atoms to be  $6 + \delta q$ (this can be accomplished straightforwardly in many codes). One then carries out the HF calculation on the parent ethylene for a series of  $\delta q$  values to determine the smallest  $\delta q$  that renders the  $\pi^*$  orbital bound (i.e., produces a negative HF orbital energy). For several values of  $\delta q$  equal to and larger than this minimum value, one then determines the HF orbital energy  $\varepsilon(\delta q)$  and plots it as a function of  $\delta q$ . For the ethylene case at hand, one obtains a plot like that shown in Figure 4.

Notice how the energy of the LUMO + 4 orbital is stabilized more strongly as a function of  $\delta q$  than are the energies of the other virtual orbitals. This is because, as shown in Figure 1, the LUMO + 4 orbital, the putative  $\pi^*$  orbital, is more highly localized near the two C nuclei while the PC orbitals reside more distant from these nuclei. Also notice that the energies of the LUMO, LUMO + 1, and LUMO + 2 orbitals become negative at approximately  $\delta q = 0.25$  and only for  $\delta q \ge 0.3$  is LUMO + 4 the lowest energy orbital. Finally, also notice how the orbital energy plots develop small negative curvatures (i.e.,



**Figure 4.** Plots of several HF orbital energies (eV) as functions of the  $\delta q$  quantity for the lowest eight virtual orbitals of ethylene. The red dots follow a quadratic interpolation to the energies of the LUMO + 4 orbital whose relevance is explained later in the text.

quadratic dependence on  $\delta q$ ) especially after they drop below  $\varepsilon(\delta q)=0$ ; we will have more to say about this matter later because it influences how we can extrapolate this data to obtain the KT estimate of ethylene's EA. In a larger, more complicated, and less symmetrical molecule containing an olefinic unit, a plot of virtual orbital energies versus  $\delta q$  would look like Figure 4 but likely would have significantly more orbital energies within which to find the desired  $\pi^*$  orbital.

The next issues to deal with include (1) whether the plot of the energy of the LUMO + 4 can be used to estimate (e.g., by extrapolation) the energy of the electron-attached olefin as it exists in the absence of the artificial stabilizing potential, (2) what, if anything, can be done to not have the energies of the PC orbitals dropping below zero, thus requiring one to use larger values of  $\delta q$  to clearly isolate/identify the  $\pi^*$  orbital, and (3) how to proceed to obtain a reliable (i.e., beyond Koopmans' theorem) estimate of the olefin's EA.

3.3.1. Koopmans' Theorem EA Estimate; How to Make It Even if It Is Not Very Accurate. Within the region of the plot where  $\varepsilon(\delta q)$  is negative ( $\delta q \ge 0.3$ ), the  $\pi^*$  attached anion is stable, and the HF orbital energy provides a valid (i.e., within Koopmans' theorem) approximation to its energy. Where  $\varepsilon(\delta q)$  is positive, the  $\pi^*$  orbital is metastable and exists within a sea of PC orbitals; here, its HF orbital energy is not a sufficiently accurate approximation to the electron-attached state. To obtain a valid value for the Koopmans' theorem energy of the  $\pi^*$ -attached state for the bare ethylene anion, one extrapolates the plot of  $\varepsilon(\delta q)$  as a function of  $\delta q$  to  $\delta q \to 0$ using data only for negative  $\varepsilon(\delta q)$  and for  $\delta q \ge 0.3$ . In Figure 4, we show a quadratic extrapolation using data only for  $\varepsilon(\delta q)$ > 0.3. This produces a KT-estimate to the EA of -3.2 eV. The actual<sup>58</sup> (i.e., experimental and from high-level theory) EA of this metastable ethylene is -1.8 eV, which illustrates what we said earlier that one needs to go beyond HF theory and include orbital relaxation and electron correlation, as we will illustrate later, to obtain a more accurate result.

3.3.2. Stabilization of the PC Orbitals is a Problem. It would have been preferable if the artificial stabilization potential had less strongly stabilized the PC orbitals because

then the  $\varepsilon(\delta q)$  versus  $\delta q$  data for the LUMO + 4 orbital could have been used to lower  $\delta q$  values (e.g., near  $\delta q = 0.2$  as can be seen in Figure 4), where the LUMO + 4 orbital's energy first becomes negative. This would make more reliable the extrapolation to  $\delta q \rightarrow 0$ . We will have more to say later about how one might avoid this problem but, for now, we only want to recognize its existence.

3.3.3. Including Electron Correlation after Stabilization Has Allowed One to Identify the Desired  $\pi^*$  Orbital. As explained earlier, when using any electronic structure method that includes electron correlation effects to study an electron attachment event, it helps to have the singly occupied spinorbital be that with the lowest HF orbital energy. This means that one should focus on  $\varepsilon(\delta q)$  values only with  $\delta q \ge 0.3$  when attempting to identify the  $\pi^*$  orbital and to use this orbital if one wants to move beyond the HF level to include electron correlation. For example, one can use the HF orbitals and orbital energies resulting from a series of HF calculations with  $\delta q \geq 0.3$  to carry out CC calculations on the parent olefin and on the  $\pi^*$ -attached olefin. That is, one carries out one CC calculation on the species having an excess electron in the (stabilized)  $\pi^*$  orbital and a second CC calculation on the species in the absence of the excess electron; the energy difference is the CC-EA at that value of  $\delta q$ . Doing so generates a series of EAs at various  $\delta q$  values as plotted in Figure 5. Extrapolating these EA data (again using a quadratic fit) back to  $\delta q \rightarrow 0$ , one obtains an estimate of -2.75 or -2.28 eV for the EA of the metastable ethylene (depending on the atomic orbital basis set used).

In Figure 5, we show two such plots, one derived from CC calculations using the  $6-31++G^{**}$  basis set detailed in the Methods section and the second from CC calculations using the aug-cc-pVTZ basis set also described in the Methods section. The former extrapolates to an EA of -2.75 eV and the latter to an EA of -2.28 eV. We offer two data sets to illustrate the differences that can occur when one chooses one or other commonly employed atomic orbital bases.

This charge stabilization method is a good one to find and characterize (by energy) the kind of  $\pi^*$  orbitals discussed here. We should note that it can also be used to treat  $\sigma^*$  orbitals as we have done in treating electron-attached cleavage of disulfide bonds. It can also be used to characterize the  $\pi^*$  orbitals of  $\pi\pi^*$  excited states that have energies above the ionization threshold. In that case, one could carry out TD-DFT or CIS calculations on the olefin at a range of appropriate  $\delta q$  values (i.e.,  $\delta q \ge 0.3$  for this example). These excitation energy data can be plotted versus  $\delta q$  and extrapolated to  $\delta q \rightarrow 0$  to obtain an estimate of the olefin's  $\pi\pi^*$  excitation energy.

There is another device similar to the nuclear charge stabilization method that we believe is worth including in this discussion because it is rather straightforward to implement within many widely available electronic structure codes. This device is based on the assumption that surrounding the metastable electron-attached species with solvent molecules that occupy regions ranging outward from the van der Waals (vdW) surface of the parent molecule will differentially stabilize the valence  $\pi^*$ -attached state relative to the states in which the extra electron resides in a PC orbital that likely resides primarily outside the vdW surface. In many electronic structure codes, tools such as the polarized continuum model<sup>19–21</sup> (PCM) or more sophisticated methods can be used to simulate the influence of such a solvation environment. Based on the basic Born model<sup>59</sup> for solvation by a dielectric



**Figure 5.** Plots of  $EA^{CC}$  vs  $\delta q$  obtained using the 6-31++G\*\* basis set (a) and using the aug-cc-pVTZ basis set (b). In both plots, a quadratic fit was employed.

medium having dielectric constant  $\varepsilon$ , the electronic energy of the anion is expected to be lowered by an amount  $\Delta E$  (in eV) given by

$$\Delta E = -14.4 \frac{Q^2}{2R(\text{\AA})} \left(1 - \frac{1}{\varepsilon}\right) \text{eV}$$
(3)

where Q is the charge on the electron-attached species (unity for the olefin anions considered here), R is the ionic radius of the anion in Å, and  $\varepsilon$  is the solvent's static dielectric constant. This model suggests that if one were to imbed the metastable species in a solvent of sufficient dielectric strength, the localized  $\pi^*$ -attached state could be stabilized to an extent to render it electronically stable. This, in turn, suggests that if one were to compute the electronic energy of this state (relative to that of the parent species) for a range of  $\varepsilon$  values for which the electron-attached state is stable and then plot the energies versus  $1/\varepsilon$ , one should observe a near-linear dependence. If so observed, this linear plot can be extrapolated back to  $\varepsilon \rightarrow 1$  to estimate the energy of the metastable state in the absence of solvation.

Clearly, this procedure is similar in its implementation to the nuclear charge stabilization method discussed earlier. It has been used<sup>60,61</sup> successfully to estimate EAs of a wide variety of organic molecules and two examples of the kind of plot explained above are shown in Figure 6 for an electron attached to the  $\pi^*$  orbital of ethylene. Here, EA is the energy of the anion state relative to that of the neutral (positive EA for a bound state).

These results illustrate that one should be careful to explore different atomic orbital basis sets when using this method. The KT extrapolation plot for the 6-31++G\*\* basis that has been used throughout most of this paper's work and for the KT extrapolation for the aug-cc-pVTZ basis described in the Methods section are shown in Figure 6a,b, respectively. They are quite similar and extrapolate to approximately the same value. However, as can be seen in Figure 6c, the 6-31++G\*\* basis' CC extrapolation was not nearly as reliable as that for the aug-cc-pVTZ basis shown in Figure 6d. The latter result gave a final CC EA estimate of -2.10 eV, which is much closer to the experimental result<sup>58</sup> of -1.8 eV than is either the KT estimate. For smaller values of the dielectric constant, when we attempted to use the (charge-stabilized) LUMO from the 6- $31++\hat{G}^{**}$  basis' calculation as the "guess" for the singly occupied orbital of the ethylene anion in the CC calculation, it turned out that the energy in this electron-attached calculation was higher than the energy of the corresponding parent. This was surprising given the fact that the KT-level results behaved as expected even for dielectric constants near 2.0. On the other hand, for the aug-cc-pVTZ basis, using its (stabilized) LUMO as the guess for the singly occupied orbital of the electronattached species produced an energy below that of the parent for a wide range of dielectric constants. As a result, we feel more confident in using the data in Figure 6d to arrive at our final CC-EA estimate of -2.10 eV.

3.4. Weakly Bound LUMO Might Occur and Be a Dipole-Bound Orbital Rather than the Orbital One Is Seeking or Rather than a PC Orbital. Earlier, we saw that for ethylene as treated using the basis functions employed here, the LUMO through LUMO + 3 HF orbitals was of the PC kind and had positive orbital energies. If the olefin contained substituents that made it highly polar, a different kind of electron-bound state can arise, and one needs to know how to handle it. To illustrate, we consider  $(NC)_2C=CH_2$  which has a dipole moment of 5.13 Debyes. Such highly polar molecules are known<sup>9,10</sup> to produce the so-called dipole-bound anions in which the extra electron is bound into an orbital on the dipole's positive end as shown in Figure 7 for the dicyano-ethylene case.

In such situations, one might find a LUMO of the parent that is bound (i.e., has a negative orbital energy) in the absence of any stabilizing charge or stabilizing dielectric, but it would be incorrect to assume that this LUMO is the desired  $\pi^*$  orbital, so again one has to examine more of the virtual orbitals to locate a candidate  $\pi^*$  orbital. This LUMO is not a PC orbital; it is a real bound orbital, but it is not the  $\pi^*$  orbital. It turns out that it is also possible for neutral molecules containing highly polarizable groups to find weakly bound orbitals whose binding arises primarily from the electron-molecule polarizability potential. In the search for the desired  $\pi^*$  orbital, there is not much more to do but to be aware of the presence of this dipole-bound or polarization-bound orbital



**Figure 6.** Plots of EA<sup>KT</sup> vs  $1/\varepsilon$  for results obtained using the 6-31++G<sup>\*\*</sup> basis (a) and using the aug-cc-pVTZ basis (b) and plots of EA<sup>CC</sup> vs  $1/\varepsilon$  for results obtained using the 6-31++G<sup>\*\*</sup> basis (c) and using the aug-cc-pVTZ basis (d).



**Figure 7.** Dipole-bound LUMO for neutral  $(CN)_2C=CH_2$  having an orbital energy of  $\varepsilon(a_1) = -0.019$  eV obtained with the 6-31++G\*\*+4(sp)2d basis described in the Methods section. The outermost contour of this orbital contains 88% of electron density.

and then to proceed as described earlier to continue one's search and to guide the calculation to populate the desired orbital. On using the charge stabilization method to find that orbital, one should use data only for  $\delta q$  values beyond which the desired  $\pi^*$  orbital's energy is negative and more negative than the energy of the dipole-bound orbital and of any PC orbitals.

**3.5. Rydberg Orbitals Can Also Occur and Complicate Matters.** If the parent molecule has positively charged groups in it, the LUMO (and more LUMO + K orbitals) can turn out to be rather strongly bound Rydberg orbitals rather than the orbital one is seeking or rather than a PC orbital. In Figure 8, we show the lowest energy Rydberg orbital that is attached to a protonated lysine side chain of a polypeptide as studied<sup>62</sup> in one of our efforts to study how electron attachment can fragment polypeptides.

These Rydberg orbitals typically have very substantial HF electron binding energies (ca. 1-4 eV) often making them the LUMO of such positively charged molecules. As with the dipole-bound orbitals, there is not much more to do but to be aware of the presence of such Rydberg orbitals and then to



Figure 8. Ball and stick depiction of the left half of the doubly protonated polypeptide.  $(H-Lys-Ala_{20}-SS-Ala_{20}-Lys-H)^{2+}$ . Adapted from Figure 1 in ref 62 with permission of the American Chemical Society.

proceed as described earlier in the search for a  $\pi^*$  virtual orbital (e.g., using the charge stabilization method) to continue one's search.

It should be mentioned that the Coulomb potential arising from the positively charged group(s) as shown in Figure 8 does some of the work in stabilizing low-energy  $\pi^*$  virtual orbitals. For this reason, it might turn out that the charge stabilization or dielectric stabilization too is not necessary to render the desired  $\pi^*$  orbital bound. This phenomenon is discussed in ref 62, where we treated electron attachment to peptide backbone amide OCN  $\pi^*$  orbitals that facilitated by the presence of protonated sites in the peptide. It is also worth emphasizing that, although we are focused here on how to identify  $\pi^*$ orbitals, the tools we are describing can be used for  $\sigma^*$  orbitals as well. For example, in ref 62, we also discuss the attachment of an electron to the S–S  $\sigma^*$  orbital of a large polypeptide similar to that illustrated in Figure 8 as well as into amide OCN  $\pi^*$  orbitals along the peptide backbone. For such species, the  $\pi^*$  orbitals have negative EAs of ca. -2.5 eV, while the S–S  $\sigma^*$  orbital has a negative EA of ca. –1.0 eV; the point is that  $\sigma^*$  orbitals are not always high-energy orbitals.

3.6. Dealing with the Problem of the Nuclear Charge Stabilization Tool Producing Stabilized  $\pi^*$  and PC Orbital Energies Varying Non-linearly with  $\delta q$ . The  $\delta q$  positive charges added to the carbon nuclei produce an artificial species that has a net positive charge. We have already seen (Figure 4) how this can cause some of the PC orbitals to be stabilized to an extent that their HF orbital energies become negative. We have explained how this can hinder one's ability to extrapolate the energy of the  $\pi^*$ -attached state to  $\delta q \rightarrow 0$ .

The Coulomb stabilization potential can also give rise to non-linearity in the  $\varepsilon(\delta q)$  versus  $\delta q$  plots as one also sees clearly in Figure 4. The stabilizing potential that causes the system to have a net positive charge generates a long-range Coulomb attraction for the extra electron, which is well known to be capable of generating bound Rydberg-like (RL) states. Such bound RL states might or might not arise in a particular calculation depending on how many diffuse atomic basis functions are employed. The electron binding energies of RL states are known to vary quadratically with the positive charge  $\delta q$ , which likely plays a role in causing the stabilized orbital energies appearing in Figure 4 to display (small) quadratic dependences on  $\delta q$ . In Figure 9, we show a plot of the states that arose for ethylene similar to that shown in Figure 4 but in which we have calculated the HF orbital energies for a wider range of  $\delta q$  values.

Here, one can see clearly that the orbital energies (including that of LUMO + 4) develop quadratic dependences at larger



**Figure 9.** Plots of several HF orbital energies (eV) as functions of  $\delta q$  for the lowest eight virtual orbitals of ethylene.

 $\delta q$  values. This is why we used a quadratic functional form to perform the extrapolations discussed earlier when using the charge stabilization method.

The appearance of PC states that have become bound (and might have developed quadratic  $\delta q$  dependence) does not necessarily mean one cannot make use of the charge stabilization method, but it does introduce complications that need to be overcome. If they arise, one needs to make sure to use as the assumed occupied spin-orbital the charge-stabilized  $\pi^*$  orbital and to use energy data to extrapolate only for  $\delta q$  values for which the  $\pi^*$  orbital lies below the stabilized PC orbitals. As illustrated earlier, this constraint can produce limitations on the accuracy of the extrapolated energy if the  $\pi^*$  orbital is not the lowest orbital until rather large  $\delta q$  are reached. Moreover, the presence of small quadratic dependences in the plots makes it appropriate to do the energy extrapolation using a quadratic functional form.

3.7. Can Stabilization of the PC Orbitals Be Avoided? There have been several approaches introduced aimed at stabilizing the desired valence  $\pi^*$  orbital without stabilizing too much the PC orbitals. Two of us have carried out calculations  $^{63}$  on molecular anions that have been rendered stable by placing them inside a so-called "trap" consisting of two highly polar molecules whose dipoles are directed inward toward the trapped anion. Of course, this device requires one to add complexity to the calculation due to the presence of the electrons and nuclei of the polar molecules used to form the trap. Recently, Sajeev introduced a so-called continuumremover potential,<sup>64,65</sup> which adds to the electronic Hamiltonian a (one-electron) box potential that is negligible in the valence region and repulsive outside the valence region. This in effect pushes the PC orbitals to higher energy, thus removing them from the energy neighborhood of the  $\pi^*$  orbital. We mention that the remover potential is a one-electron operator because such an operator is straightforward to implement within the electronic structure code. White et al.<sup>66</sup> have also introduced new one-electron potentials to use in a similar manner.

Within the framework of the charge stabilization method, one can add positive charges  $\delta q$  to the two ethylene C nuclei and add offsetting negative charges  $-\delta q/2$  to each of the four

H nuclei. Doing so generates an artificial parent molecule that is neutral for which the presence of the partial negative charges are designed to, in combination with the positive partial charges, not stabilize (much) the PC HF orbitals and not give rise to RL states. In Figure 10, we show the results of such a calculation on neutral ethylene obtained with the 6-31+ +G(d,p) basis set as specified in the Methods section.



**Figure 10.** Plot of the HF orbital energies of the LUMO through LUMO + 7 orbitals of ethylene as functions of the partial charge parameter  $\delta q$ .

This provides a successful example of using the mixed charge stabilization method to keep the PC orbitals energetically away from the desired  $\pi^*$  orbital but notice how the energy of the LUMO + 4 orbital still displays some quadratic dependence, which should be used in the extrapolation process. We should caution, however, that if the magnitudes of the partial charges become too large, they can distort the shapes and energies of the occupied orbitals to an extent that is harmful. We experienced this in the example discussed above when we allowed  $\delta q$  to exceed 2.3.

In Figure 11, we show another example of how one can separate the PC orbitals from the valence  $\pi^*$  orbital in which

the Sommerfeld group<sup>67</sup> used charge-stabilized methods and a new method they introduced to try to keep the PC orbitals out of the way. In that work, they studied several low-energy states arising from attachment of an electron to a virtual orbital of a model potential.

In the left panel, we show results obtained using the charge stabilization method (here  $\xi$  is used to describe the strength of the stabilization potential), and one can see that the Coulomb stabilizing potential produces substantial stabilization to the PC orbitals as well as significant curvature. On the right panel, we show the results obtained using the so-called (oneelectron) Voronoi stabilizing potential (whose strength is characterize by  $V_0$ ) from ref 67 rather than the Coulomb stabilization. There is a clear improvement in the Voronoi data as the PC orbitals remain (mostly) above zero in energy and the curvature in the orbital energies is considerably reduced.

**3.8.** How the Lifetime of the Metastable Anions Can Be Estimated Even by Non-experts. The lifetime of a metastable electronic state of an electron-attached state is determined by the coupling between the valence range orbital (e.g., the  $\pi^*$  orbital in most of the discussion in this work) and a continuum orbital into which the electron escapes when it is ejected. As explained earlier, in most electronic structure codes, the continuum orbital is approximated by a PC function described within the finite atomic orbital basis set. If the particular basis set provides a PC orbital of the same symmetry and close in energy to that of the valence range orbital, the coupling between them can be evaluated and used to estimate the lifetime.

To illustrate, consider the orbitals and orbital energies shown in Figure 1. The  $\pi^*$  orbital energy is +2.865 eV and the PC orbital closest to it in energy is the LUMO + 3 orbital with an energy of +2.313 eV. Therefore, if the coupling strength between these two orbitals were of the order of the ca. 0.5 eV energy gap between them, they might be useful in such a lifetime calculation. Unfortunately, in this case, the fact that these two orbitals are of different point group symmetries means that their coupling will be zero, so one would not be able to estimate the lifetime using this data. In fact, none of the orbitals shown in Figure 1 are of the same symmetry as that of



**Figure 11.** Plots of energies (in atomic units equal to 27.21 eV) of the stabilized electron-attached state of a model potential (blue for  $\xi >$  ca. 1.0 (left) or for  $V_0 >$  ca. 4 (right), the red continuing to smaller  $\xi$  or  $V_0$ ) and PC states (other red curves) as functions of the strength  $\xi$  of the Coulomb potential or  $V_0$  of the Voronoi potential (reprinted from ref 67 with the permission of AIP Publishing).

 $\pi^*$ , so the set of virtual orbitals obtained with this basis set would not be of use in this regard.

Therefore, how would one then proceed? One would have to add to the atomic orbital basis a few functions that would be capable of forming one or more MOs of  $b_{2g}$  symmetry (e.g.,  $p_{\pi}$ functions on the two C atoms). This alone would not guarantee that a PC orbital of  $b_{2g}$  symmetry would have energy comparable to that of the LUMO + 4 orbital in Figure 1. To "fine-tune" the atomic basis set to generate a PC function of the appropriate energy, one would then change the exponents of the diffuse basis functions that contribute strongly to the PC orbitals; this is usually accomplished by scaling all of the orbital exponents by the same multiplicative value Z. Increasing Z beyond 1.0 will radially contract the orbitals and increase their energies while decreasing Z below 1.0 will have the opposite effect. By carrying out a series of HF calculations at various Z values and plotting the HF orbital energies as a function of Z, one can generate a so-called stabilization plot,<sup>68-73</sup> two of which<sup>69,74</sup> are shown in Figure 12.

In the hypothetical stabilization plot in Figure 12a, two plateaus (e.g., the blue regions) appear (below 0.5 eV and near 1.3 eV) and suggest the existence of two metastable states. In the ethylene anion case discussed in this paper, a plateau near 2.8 eV (the energy of LUMO + 4) would occur. Each plateau is interrupted by an avoided crossing (e.g., the red regions) between two HF orbital energies-one being the energy of a valence-range ( $\pi^*$  in the ethylene case) orbital and the other a PC orbital. The PC orbitals' energies appear as the branches (e.g., the green lines) that increase strongly as the scaling factor Z is increased for the reason explained earlier.

In the stabilization plot shown in Figure 12b, four sets of dots are shown, three originating for PC states (whose energies are traced out in dashed lines) and one coming from the valence-range component of the metastable state. We offer this example to illustrate that the shapes of the curves undergoing the avoided crossing, in particular their slopes at the center and as they leave the avoided crossing, can be difficult to characterize accurately. This, in turn, limits the accuracy of the estimate one can make for the lifetime using the device described below.

In the most elementary model<sup>71</sup> from which one can estimate the lifetime of a metastable state, any avoided crossing between a valence-range and PC orbital is approximated as follows. One assumes that the energy of the valence-range orbital varies linearly with the scaling factor Z with a small slope (since the valence-range orbital is influenced less by variations in the diffuse basis functions) until it approaches an avoided crossing

$$\varepsilon_{\text{valence}} = b_1 + a_1 Z \tag{4}$$

while the PC orbital's energy also varies linearly with Z but with a larger slope as in Figure 12 (i.e.,  $a_2 > a_1$ )

$$\varepsilon_{\rm PC} = b_2 + a_2 Z \tag{5}$$

One assumes that these two linear graphs intersect at  $Z = Z_C$ where their common energy is E<sub>C</sub>. Then, one considers that these two linear functions represent the diagonal elements of a  $2 \times 2$  Hamiltonian matrix and the off-diagonal coupling between them is taken to be a constant V. The two eigenvalues of such a  $2 \times 2$  matrix can be shown to be



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Energy (eV)



Figure 12. (a) Generic stabilization plot showing how the energies (relative to the energy of the system in the absence of the excess electron) of several electron-attached states vary with the basis-extent scaling factor Z. (Reprinted from ref 69 with permission from Elsevier); (b) stabilization plot (dots) for adding an electron to a  $\pi^*$ orbital of N2 with data obtained using EOM-CC methods; dashed lines are energies of PC levels computed as electron-attached states in the absence of the N<sub>2</sub> molecule's nuclei and 14 electrons. (Reprinted

(b)

$$E_{\pm} = E_{\rm C} + \frac{a_2 + a_1}{2} (Z - Z_{\rm C})$$
$$\pm \sqrt{V^2 + \left(\frac{a_2 - a_1}{2}\right)^2 (Z - Z_{\rm C})^2} \tag{6}$$

with permission of ACS from ref 74.)

The two branches of this function are assumed to represent the avoided crossing.

Several years ago, one of us showed<sup>71</sup> that one could estimate the lifetime  $(\tau)$  of the metastable state by finding the (complex) value of Z at which one of the energy branches of eq 6 is stationary (i.e., has dE/dZ = 0) and then evaluating the

$$E_{\rm sp} = E_{\rm C} - 2iV \frac{\sqrt{a_1 a_2}}{a_2 - a_1} \tag{7}$$

It turns out that the imaginary part of this energy, which is called the half-width  $\Gamma/2$  of the metastable state's energy, is related to the lifetime of that state by

$$\Gamma/2 = 2V \frac{\sqrt{a_1 a_2}}{a_2 - a_1} = \frac{\hbar}{\tau}$$
(8)

This then is one path by which one can estimate the lifetime. One forms a stabilization plot and estimates the slopes of the two branches of an avoided crossing  $(a_1 \text{ and } a_2)$ . One then evaluates the coupling parameter V as twice the energy splitting between the two branches at their avoided crossing's closest approach  $Z_{\rm C}$  (see eq 6). Knowing the two slopes and the value of V, one can evaluate  $\Gamma/2$  and thus  $\tau$ . This path describes the most elementary means by which such lifetimes can be estimated. There also exist methods<sup>72,73</sup> in which the two branches of the stabilization plot undergoing an avoided crossing are represented by higher order polynomials in Z. However, just as with the most basic method just outlined, one has to perform the fitting and determination of the lifetime from this fit independently (i.e., on one's own). Of course, there are many alternative means for estimating lifetimes and many of them have proven to be more accurate but most of them are not yet available in commonly used electronic structure codes.

One might wonder whether the kind of plots arising in the charge or dielectric stabilization methods could be used to extract half-widths or lifetimes. The answer is yes but the technology involved is a bit more complicated than discussed above for the stabilization plot method. For example, Sommerfeld made use of the charge stabilization data shown in the left of Figure 11 to calculate such a width and lifetime using an approach that we will now briefly describe.

The key<sup>37,75–78</sup> to using the extrapolation of charge stabilization data to estimate lifetimes lies in correctly describing how the metastable state's energy evolves from bound (where EA is positive) to metastable (where EA is negative). In the region where the valence state being followed is bound, the anion's energy lies below that of the neutral, so EA is positive and, as we showed earlier, it can be extrapolated back to Z = 0 to estimate the energy of the metastable state. However, the method by which one can estimate the lifetime involves extrapolating the momentum p rather than the energy EA. When EA is negative, the kinetic energy of the escaping electron is

$$\frac{p^2}{2m_{\rm e}} = -{\rm Re}({\rm EA}) \tag{9}$$

where Re(EA) is the real part of the metastable state's EA, and the momentum is real.

When the charge stabilization method is used to render the electron-attached state stable, the plots of EA versus  $\delta q$  have significant quadratic dependence globally. However, near the point  $\delta q_0$  where EA moves from positive to negative (and thus vanishes), it varies (approximately) linearly as a function of the parameter  $\delta q$ 

$$EA = EA(\delta q_0) + s(\delta q - \delta q_0) = s(\delta q - \delta q_0)$$
(10)

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Because the momentum is related to the square root of the EA, the developers  $^{75-78}$  of this method considered how to express this square root

$$\kappa = \sqrt{EA} \tag{11}$$

as a function of  $\sqrt{\delta q} - \delta q_0 \equiv y$  in a manner that could cover both  $\delta q > \delta q_0$  and  $\delta q < \delta q_0$ . Notice that this square root is real when  $\delta q > \delta q_0$  and is imaginary when  $\delta q < \delta q_0$ . These workers decided to express  $\kappa$  as a function of y in terms of a so-called rational fraction (RF)

$$\kappa_{\rm RF}[N, N-K] = \frac{n_0 + n_1 y + n_2 y^2 + \dots + n_N y^N}{1 + d_1 y + d_2 y^2 + \dots + d_{N-K} y^{N-K}}$$
(12)

This RF is of order N in the numerator and N–K in the denominator (typically N will exceed N–K by 1 or 2 since the large- $\delta q$  behavior of the charge stabilization data shows mainly linear with some quadratic  $\delta q$ -dependence).

By using the charge stabilization graph to estimate the value  $\delta q_0$  of the coupling parameter at which the EA passes through zero, one can evaluate *y* at a set of  $\delta q$  values for which  $\delta q > \delta q_0$  and, at these same *Z* values, one can use the charge stabilization method to evaluate the corresponding real values of  $\kappa$  from the computed positive EA values using eq 11. By fitting these  $\kappa(y)$  data to the functional form in eq 12 for the real values of *y*, one can determine the  $n_k$  and  $d_k$  parameters in this equation. After doing so, one can then extrapolate to  $\delta q = 0$  by evaluating eq 12 at the imaginary value of  $y = i\sqrt{\delta q_0}$  to determine the complex value of  $\kappa = \kappa_r + i\kappa_i$ . This then allows the complex value of the metastable state's EA to be determined from eq 11 as

$$EA = \kappa_r^2 - \kappa_i^2 + 2i\kappa_r\kappa_i$$
(13)

The imaginary part of the quantity gives the half-width  $\Gamma/2$ , which, in turn, can give the lifetime.

This kind of extrapolation can be carried out using many commonly available electronic structure codes, which allow one to form a charge stabilization plot (i.e.,  $EA(\delta q) vs \delta q$ ) but one would have to implement the fitting of eq 12 independently since this step is not included in most such codes.

#### 4. CONCLUSIONS

This overview focused on explaining the challenges one faces in attempting to properly identify and make use of a desired valence virtual  $\pi^*$  or  $\sigma^*$  antibonding orbital to be used within an electronic structure calculation to study either electronattached or electron-excited states. Special emphasis was placed on situations in which the electronic state of interest is metastable with respect to electron ejection. Briefly, the takehome lessons are as follows:

- 1 The parent molecule might possess virtual orbitals that are bound but are not the desired valence antibonding orbitals. These can arise in the following situations:
  - a If the neutral molecule is highly polar, the LUMO could be bound and be a dipole-bound orbital; it would not be the desired  $\pi^*$  or  $\sigma^*$  orbital.
  - b If the molecule has positively charged groups within it, the LUMO (and more) likely will be Rydberg orbitals localized on the positive sites; these too are not the desired  $\pi^*$  or  $\sigma^*$  orbital.

In these situations, if methods that calculate separate energies for the parent and electron-attached or electron-excited species are employed, one must guide the software to not occupy these orbitals in forming the electron-attached or electron-excited wave function. Moreover, one must monitor the calculation to watch for variational collapse in which the excess electron turns out to occupy the dipole-bound or Rydberg orbital. If using a method that computes the attachment (e.g., EOM-CC) or excitation (e.g., CIS and TD-DFT) energy directly, one needs to identify the eigenvalue of the corresponding matrix that involves populating the desired  $\pi^*$  or  $\sigma^*$  orbital rather than any dipole-bound, Rydberg, or PC orbital.

- 2 When using any atomic orbital bases that include diffuse basis functions, some of the lowest unoccupied MOs of any molecule that does not have a positive EA are likely to correspond to PC orbitals; the virtual orbital most representative of the desired  $\pi^*$  or  $\sigma^*$  orbital to use in electron attachment will have an energy lying within a sea of such PC orbitals. In these situations, it is best to employ one of the valence orbital stabilization techniques described here to isolate the desired orbital. Doing so, and perhaps choosing to carry out a subsequent calculation that includes electron correlation, requires one to also extrapolate the computed EA to remove the effects of the artificial stabilization.
- 3 To obtain a reliable estimate of the energy of any electron-attached species, it is almost always necessary to carry out a calculation that treats electron correlation. Estimates based on HF or DFT orbital energies alone are usually not sufficient.
- 4 For dealing with  $\pi^*$  orbitals of excited states (e.g.,  $n\pi^*$ or  $\pi\pi^*$ ) rather than electron-attached states, one can perform TD-DFT or CIS calculations on the parent molecule, but care must be exercised to identify the eigenvalue of the corresponding matrix that involves populating the desired  $\pi^*$  or  $\sigma^*$  orbital. Alternatively, one can carry out separate calculations for the energies of the parent and excited states, being careful to make sure the excited-state calculation populates the proper antibonding orbital and does not undergo variational collapse. If the excitation energy thus obtained exceeds the energy required to remove an electron from the parent's n or  $\pi^*$  orbital, the excited state is electronically metastable. In that case, one should use one of the valence orbital stabilization methods and extrapolate the computed excitation energy to remove the artificial stabilization.
- 5 For calculating the lifetimes of the electron-attached or excited metastable states discussed here, there exist methods that can be implemented using many widely available electronic structure codes with a bit of extra effort. These include extrapolating Coulomb-stabilized energy data or varying orbital exponents of diffuse basis functions to form a stabilization plot. These steps require one to carry out a portion of the calculation beyond what is included in most electronic structure codes using the tools described here.
- 6 It will prove beneficial to remain informed about developments that use more sophisticated (and likely more accurate) methods than those detailed in this work. Those methods also offer direct paths to

estimating the lifetimes of electronic states that are metastable, which one may find to be of much use. Although they are not yet available in most commonly used software, we believe that they will be within years and not decades.

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