

## Comments on Koopmans' Theorem and Electron Relaxation with Valence Ionization

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The electron relaxation energy,  $E_R$ , is a well-recognized limitation of Koopmans' approximation for ionization energies. Several characteristic aspects of  $E_R$  for first ionizations of atoms are discussed. It is shown that (1) Slater's screening model gives good account of the basic trends in  $E_R$  with valence ionizations of main-group atoms but fails for d electron ionizations of transition metals, (2) the relatively large  $E_R$  for ionization of 3d electrons is associated with the 3d shielding of 3s and 3p electrons (these relaxation characteristics help to clarify the filling of the 4s and 3d orbitals in the periodic table), and (3) there is more than a proportional decrease in  $E_R$  when the valence density removed from an atom is less than a complete electron (this indicates that the intraatomic portion of  $E_R$  will be less for ionization from a delocalized orbital than from a localized orbital).

The ionization energies of atoms and molecules are associated with many aspects of chemistry, including certain thermochemical cycles, models of electronegativity, and parameterization schemes for semiempirical molecular orbital theories. Koopmans' theorem<sup>1</sup> relates ionization energies to electron orbital energies in the Hartree-Fock model and thus provides a theoretical framework for interpreting the associated physical and chemical properties in terms of ground-state electronic structures. As a result, Koopmans' theorem has had either a direct or implied influence on many current concepts and models of chemical behavior.

The description of any molecular property or chemical process in terms of ground-state structure is limited by the approximate representation of the excited or final state. In the case of Koopmans' theorem this limitation arises from the assumption that, when an electron is removed from an atom or molecule, the remaining charge distribution does not change. In fact, the remaining charge distribution is contracted or reorganized as a result of the decrease in electron-electron repulsions.<sup>2</sup> The difference in energy between the positive ion with "frozen" orbitals (Koopmans' ion) and the positive ion with optimized orbitals (SCF ion) is termed the relaxation energy,  $E_R$ .

Because of our interest in the high-resolution valence-photoelectron spectroscopy and electronic structure of transition-metal complexes, we have been directly concerned with understanding the limitations of Koopmans' approximation. This has led us to a fundamental theoretical investigation of the relaxation process with valence ionization. One aspect of this study has involved different ab initio model calculations of the electronic structure of atoms and ions.<sup>3</sup> We wish to report here some features of the relaxation energy that have been revealed by this work. Our developments have been assisted by the numerous studies of electron relaxation associated with core ionization and the Auger process.<sup>4</sup> A particularly excellent presentation of these concepts along the lines of the present discussion has been provided by Martin and Shirley.<sup>5</sup> It should also be noted that several calculational

Table I. Shielding Factors  $S_{nl,n'l'}$ 

$nl^d$		$n'l'$			
		3s	3p	3d	4s
3s	a	0.35	0.35	0	0
	b	0.25	0.25	0.34	0.08
3p	a	0.35	0.35	0	0
	b	c	0.38	0.33	0.05
3d	a	1.0	1.0	0.35	0
	b	c	c	0.27	0
4s	a	0.85	0.85	0.85	0.35
	b	c	c	0.84	0.10

<sup>a</sup> Slater's rules.<sup>7b</sup> <sup>b</sup> Clementi and Raimondi.<sup>11</sup> <sup>c</sup> Combined in single term for all inner electrons. <sup>d</sup> Shielded electrons.

alternatives to Koopmans' approximation have been put forward.<sup>6</sup>

Many of our results on  $E_R$  are easily understood in terms of Slater's concept of electron shielding and effective nuclear charges.<sup>7</sup> In this model the origin of the electron relaxation energy follows from the different total electron shielding in the positive ion compared to the neutral atom. The total shielding of each electron from the nucleus is defined as the sum of the individual electron-shielding factors from all other electrons. This may be written as eq 1 where  $S_{nl,n'l'}$  is the extent

$$S_{nl} = \sum_{n'l'} (N_{n'l'} S_{nl,n'l'}) - S_{nl,nl} \quad (1)$$

an electron with  $[n,l]$  quantum numbers is shielded by one electron with  $[n',l']$  quantum numbers, and  $N_{n'l'}$  is the number of electrons with these quantum numbers (subtracting  $S_{nl,nl}$  eliminates an electron shielding itself). Some examples of shielding factors that will prove useful are given in Table I. Similar to the development by Snyder for core-electron binding energies,<sup>8</sup> a general expression for the relaxation energy (in Rydbergs) in this model is

$$E_R = \sum_{nl} (N_{nl}^+ / n^2) [S_{nl}^+ - S_{nl}]^2 \quad (2)$$

where  $N_{nl}^+$  and  $S_{nl}^+$  correspond to the orbital occupations in the positive ion. This equation indicates that only those shells that are shielded by the electron to be removed contribute to the relaxation energy, since the term vanishes if the shell is shielded by an equivalent amount in both the neutral atom and the positive ion. According to Slater's rules for screening factors an electron does not shield electrons that are in deeper shells, so only electrons that are in the same shell as the

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- (3) Details of this work will be published elsewhere.
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- (6) For leading references see: (a) vonNiessen, W.; Dierckson, G. H. F.; Cederbaum, L. S. *J. Chem. Phys.* 1977, 67, 4124. (b) Reference 17, p 305.
- (7) (a) Slater, J. C. *Phys. Rev.* 1930, 36, 57. (b) See for instance: Huheey, J. E. "Inorganic Chemistry"; Harper and Row: New York, 1972; p 40.
- (8) Snyder, L. C. *J. Chem. Phys.* 1971, 55, 95.

electron to be removed, or in outer shells, will experience relaxation. In the case of core ionizations  $E_R$  is generally dominated by the large number of electrons in outer shells that are very effectively shielded from the nucleus by the core electron.

In the case of valence-electron ionizations there are no outer-shell electrons to relax, so only the term for intrashell relaxation need be considered. If  $N_{\text{valence}}$  is defined as the number of electrons in the valence shell (according to Slater's grouping of orbitals) of the neutral atom, eq 2 is reduced to eq 3. The numerical factor of 0.35 follows from recognizing

$$E_R = (N_{\text{valence}} - 1)(0.35/n) \quad (3)$$

that the total shielding of an electron remaining in the valence shell is reduced by 0.35 (0.30 if  $n = 1$ ) when one valence electron is removed. Equation 3 simply says that the total electron relaxation energy is proportional to the number of electrons remaining in the valence shell multiplied by a term that is related to the change in shielding of each electron.

Equation 3 suggests periodic trends in  $E_R$  that are consistent with the results of Hartree-Fock-Slater and other calculations of these relaxation energies.<sup>4f,k,l</sup>  $E_R$  decreases going down a column of the table because of the increase in principal quantum number  $n$  in eq 3.  $E_R$  is very low for the first ionization of group 1A elements, where  $(N_{\text{valence}} - 1) = 0$ , and  $E_R$  increases from left to right across a row of the periodic table. The change in  $E_R$  between atoms of successive groups is indicated to be  $(0.35/n)$ .<sup>2</sup> It is interesting to compare this prediction with the results of Hartree-Fock calculations on the atoms and ions. This comparison is not completely straightforward because of complications caused by certain open-shell states and electron configurations of the atomic species. These configurations lead to a slightly nonuniform increase in  $E_R$  from left to right across a row of the periodic table, just as there is also a nonuniform increase in the ionization energies. However, the average change in  $E_R$  between atoms in successive groups of the first three rows of the periodic table<sup>9</sup> compares nicely with the predictions of Slater's shielding factors, as shown in Table II.

Evidence has been accumulating in recent years that exceptionally large relaxation energies may accompany the valence d ionizations of transition metals, especially metals in organometallic complexes.<sup>10</sup> A striking example is provided by the case of ferrocene. Independent theoretical studies<sup>10a,b</sup> indicate that the first ionizations of ferrocene, at about 7 eV, are associated with orbitals with high metal d character and involve relaxation energies between 6 and 7 eV. The next ionizations of ferrocene, near 9 eV, primarily involve carbon  $p_\pi$  orbitals of the cyclopentadienyl rings, and the relaxation energies are less than 1 eV. Such large differences in relaxation energy for different valence orbitals can lead to serious problems in the chemical interpretation of electronic structure. Other estimates of  $E_R$  for 3d ionization of discrete transi-

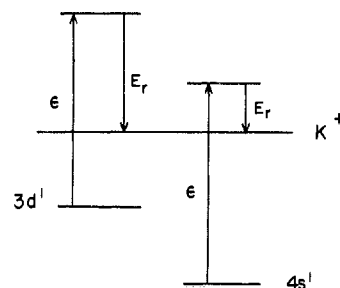


Figure 1. Relationship of the eigenvalues and relaxation energies of the 3d<sup>1</sup> and 4s<sup>1</sup> configurations to the positive-ion state of potassium.

tion-metal atoms range from about 2 eV for titanium to more than 5 eV for copper.<sup>4k,l,10b,c,h</sup>

Equation 3 indicates that  $E_R$  should be large for metals to the right of the row because of the large number of valence electrons that remain in the shell. However, the equation fails to account for the full magnitude of  $E_R$ , especially for the early transition metals. This limitation of eq 3 can be traced to the inadequacy of Slater's rules for screening factors of d electrons. Table I contains the screening factors derived by Clementi and Raimondi from their "best atom" SCF calculations.<sup>11</sup> These factors show that the 3d electrons shield the 3s and 3p electrons at least as effectively as they shield the other 3d electrons. This indicates that the 3s and 3p electrons should be included in the same shell as the 3d electrons when 3d ionization is discussed, and  $N_{\text{valence}}$  in eq 3 should range from 9 to 18 electrons instead of from 1 to 10. If eq 2 is used with Clementi and Raimondi's screening factors to estimate  $E_R$  for 3d ionization of transition metals, a reasonable agreement with other calculations of  $E_R$  is obtained.

This analysis provides a relatively simple interpretation of the filling and emptying of the 4s and 3d orbitals, which continues to be a source of confusion in the teaching of atomic electronic structure.<sup>12</sup> Much of the confusion arises from thinking that the most stable electronic state of the atom corresponds to occupying the most stable orbitals. This ignores the effect of electron-electron repulsions. For instance, when the electronic configurations of the elements in the periodic table are built up, the 4s orbital is occupied before the 3d even though the 3d orbital eigenvalue is slightly more stable than the 4s orbital eigenvalue. The major difference between electrons in the 3d and 4s orbitals is that the 3d electrons shield the 3s and 3p electrons, and this shielding destabilizes the total energy for that electronic state. The relationship between the common positive ion for the two configurations, the orbital eigenvalues, and the relaxation energies is illustrated in Figure 1. The figure shows that if two different atomic states can be linked to a common state through an ionization process, then knowledge of the appropriate eigenvalues plus relaxation energies allows prediction of the relative stability of the states.<sup>13</sup> It is worth noting that the state of sodium with a neon core and one electron in a 3d orbital is more stable than the state with one electron in the 4s orbital.<sup>12</sup> These states of sodium have no 3s and 3p electrons.

The relaxation of atomic electron density is also a contributing factor to  $E_R$  for valence ionizations of molecules. It is instructive to view  $E_R$  for molecular ionizations in terms of contributions from interatomic and intraatomic portions (eq 4). This is a natural separation for core ionizations and has

$$E_R = E_R^{\text{interatomic}} + E_R^{\text{intraatomic}} \quad (4)$$

been discussed in several papers.<sup>14</sup> The interatomic term

(9) Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* 1974, 14, 177. Groups 6 and 7 are not included in this average because of large errors in using the orbital eigenvalue to predict the energy of the frozen-orbital positive ion for these configurations. If these groups were included, the corresponding values in Table II would be, for  $n = 2$ , 0.47, for  $n = 3$ , 0.19, and, for  $n = 4$ , 0.14.

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(13) Electron correlation and relativistic effects may also influence the result.

Table II. Average Change in  $E_R$  between Successive Atoms (eV)

	$n = 2$	$n = 3$	$n = 4$
Slater's rules	0.42	0.19	0.10
Hartree-Fock <sup>9</sup>	0.42	0.17	0.13

represents a rearrangement of the molecular electron density that tends to delocalize the positive potential hole of the ion. The interatomic relaxation is generally expected to be largest for removal of an electron from a localized orbital because of the flow of remaining electron density toward the localized positive hole.

The intraatomic term represents the energy of relaxation of atomic electron densities toward their cores. This relaxation is due to loss of atomic valence electron density according to the positive hole distribution in the molecular ion. In molecular orbital terms this distribution might be represented as the atomic composition of the molecular orbital from which the electron is removed. The total intraatomic relaxation energy may be expressed as the sum of the individual atomic relaxations.

$$E_R^{\text{intraatomic}} = \sum_i^{\text{atoms}} E_R^i(F_i) \quad (5)$$

In this equation  $F_i$  represents the fractional amount of valence-electron density lost from atom  $i$ , and  $E_R^i(F_i)$  is the corresponding energy of relaxation of the electrons remaining on atom  $i$ . Generalizing eq 3 for this fractional electron loss gives eq 6. It can be seen that if  $F_i = 1$  (completely localized

$$E_R^i(F_i) = (N_{\text{valence}} - F_i)(0.35F_i/n)^2 \quad (6)$$

molecular orbital), then  $E_R^i(F_i) = E_R(\text{atomic})$ . The quantity  $(N_{\text{valence}} - F_i)$  represents the amount of electron density which remains on the atom to relax, and this density is multiplied by a factor related to the change in shielding of this density.

We have shown the functional form of this equation to be correct with model ab initio atomic calculations on the helium atom by using program POLYATOM.<sup>16</sup> The 1s function of He was first represented in a basis of six Gaussian functions.<sup>17</sup> Calculations were then performed with fractional occupations of the 1s orbital and with the total electron-electron interactions reduced appropriately. The relaxation energy was determined as the energy difference between the frozen orbital (from the neutral atom) and optimized orbital representations of the ions with fractional occupations. The dependence of  $E_R$  on  $F$  is exactly represented by eq 6 with a shielding factor of 0.335. A plot of this dependence is shown in Figure 2.

It is important to note from eq 6 that  $E_R$  is not a linear function of  $F$  as indicated in other papers.<sup>4,5</sup> The  $F^2$  dependence in eq 6 means that as less electron density is removed from an atomic orbital, the remaining density will undergo a less than proportional amount of relaxation. For instance, if  $F = 0.5$  (loss of half an electron, as in the orbital of a homonuclear diatomic), the remaining density  $(N_{\text{valence}} - F)$  experiences one-fourth rather than one-half of the atomic relaxation ( $F = 1$ ). A plot comparing atomic  $E_R$  values for fractional density loss ( $E_R(F)$ ) to that for the loss of a single electron ( $E_R(1)$ ) is shown in Figure 2. If  $E_R$  were linearly

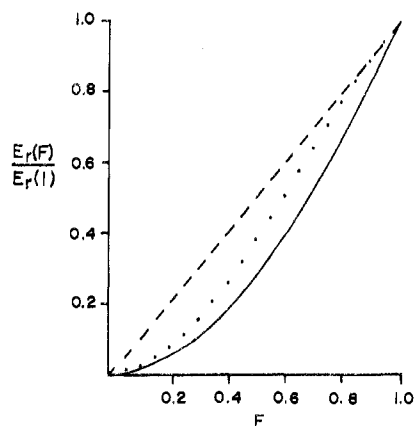


Figure 2. Comparison of relaxation energies for fractional loss of valence-electron density to loss of a complete valence electron. The dotted line represents the case of helium and was obtained from both eq 6 and ab initio calculations. The solid line represents the neon configuration. The dashed line would result if the relaxation were directly proportional to the amount of valence density removed.

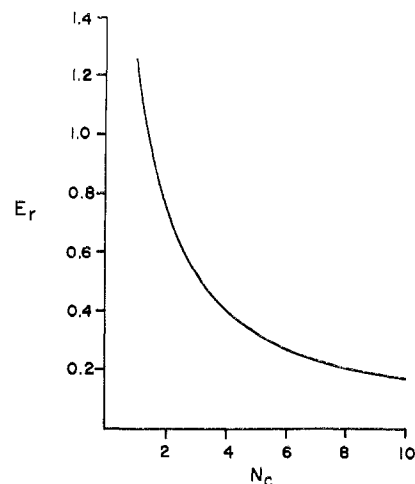


Figure 3. Intraatomic relaxation energy vs. the number of carbon atoms contributing equally to a delocalized molecular orbital.

proportional to  $F$ , the dashed line would result.

Since  $E_R(F)$  is always proportionately less than indicated by the fractional loss of electron density from a center, the intraatomic relaxation for ionization from a molecular orbital spread over several centers is expected to be less than from an orbital on a single center. Thus, like the interatomic term in eq 4, the intraatomic term also indicates smaller relaxation energies for ionizations from delocalized orbitals.<sup>10g,h,f</sup> This point can be illustrated with the example of an orbital spread equally over a number of carbon centers. If  $N_c$  is the number of carbon centers, then  $F$  for each center is  $1/N_c$ . Combining this information with eq 5 and 6 gives

$$E_R^{\text{intraatomic}} = N_c E_R^c \left( \frac{1}{N_c} \right) = \frac{1}{N_c} \left( N_{\text{valence}} - \frac{1}{N_c} \right) \left( \frac{0.35}{n} \right)^2$$

Figure 3 shows that  $E_R^{\text{intraatomic}}$  decreases rapidly as the orbital becomes more delocalized. An interesting corollary to this point is that, all other factors being the same, the most stable state of the positive ion will be the one with the most localized orbital positive hole, because this will be the state with the greatest relaxation energy from the Koopmans ion.

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