Energy and lifetime of O^{2-} from analytic continuation of isoelectronic bound states

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We offer a method for determining the stability of dinegative ions for isoelectronic series exhibiting a bound singly charged anion. Nonlinear variational ground state energies obtained with bound, multiconfigurational wavefunctions are followed above the first ionization threshold as the nuclear charge ($1/\lambda$) is decreased. Resonance energies and widths for physical states are constructed by analytically continuing the energy around a singularity at a nonphysical $\lambda=\lambda^*$. Results for the Ne isoelectronic series predict an O^{2-} resonance state at 5.38 eV (width = 1.3 eV) above the $O^- + e^-$ continuum threshold. The marked O^{2-} instability suggests that estimates of the O^- electron affinity, arising from thermochemical Born–Haber cycles, may require quantum corrections. We also discuss several chemical systems for which the method will be useful and which may lead to predictions of bound states existing in the continuum.

I. INTRODUCTION

Recent investigations[1–3] of the helium isoelectronic series have supported the original contention,[4] based on analysis of the Z^{-1} ($\equiv\lambda$) perturbation series, that the ground state energy $E(\lambda)$ penetrates into the first ionization continuum as λ is increased above $\lambda_c = 1.0975$. While it remains possible that $E(\lambda)$ has a weak singularity at λ_c, the behavior of the energy in the region $\lambda > \lambda_c$ appears to be most strongly influenced by a singularity at $\lambda^* = 1.1184$.[4,5] The exact nature of this latter singularity is not known, but its leading term is most likely[4] a branch point of order $\cong\frac{6}{5}$. Variational estimates[2] of $E(\lambda)$ obtained with sufficiently accurate wavefunctions of finite parametrization in general penetrate into the continuum and end at a branch point singularity of leading order $\frac{3}{2}$, thus indicating that branch point behavior in the exact energy may well be a justified presumption.

The apparent stability of the two-electron ^1S ground state energy in the region $\lambda_c < \lambda < \lambda^*$ suggests the existance of an exact bound stationary state (i.e., with infinite lifetime) solution to the nonrelativistic Schrödinger equation embedded in the singly ionized continuum of the same symmetry. While the absence of mixing between this proposed bound state and the adjacent continuum seems contrary to the usual formulation of scattering resonances, it has been known[6] for some time that certain bounded local potentials can support stationary states above the ionization threshold.[7] The phenomenon of a bound state crossing over into a continuum as a single parameter in the potential is varied has been described in mathematical detail for several model problems by the present authors.[8]

Explicit inclusion of the interaction of a variationally determined wavefunction with the ($1s\ ks$) ^1S continuum, or alternatively the determination of a scattering resonance by techniques such as the close-coupling approximation[9] or the stabilization method[10] would necessarily predict a finite lifetime for the state. The existance of a true bound state in the continuum, however, would be manifest by the *vanishing* of a calculated resonance width as successively higher degrees of accuracy were employed.

A rigorous proof that the two-electron ground state does remain stable in the continuum for $\lambda_c < \lambda < \lambda^*$ would not have direct physical consequences since measurable species do not exist for $\lambda > 1$. In systems with $n > 2$ electrons, however, the possible existence of a continuum bound state has considerable importance in the prediction of stability for ground states of doubly-charged negative ions in isoelectronic series having bound singly charged anions. If λ^* for an n-electron system occurred at a value larger than that of the dinegative ion [$\lambda = (n-2)^{-1}$] then we would expect this ion to be long-lived, with eventual decay resulting from either coupling to the radiation field or a spin-orbit induced autoionization. We also acknowledge the possibility that the dinegative ion might be stable below the ionization threshold.

If instead λ^* were smaller than $(n-2)^{-1}$ (λ for the dinegative ion), evidence that continuum bound states exist for nonphysical $(n-1)^{-1} < \lambda < (n-2)^{-1}$ could be identified by comparing the observed scattering width of the doubly-charged compound state with that obtained from the imaginary part of the energy $E(\lambda)$ upon analytic continuation of this eigenvalue around the singularity at λ^*. Thus a knowledge of λ^* for series with bound singly-charged anions would be useful for establishing the stability of the corresponding dinegative ions. We exclude consideration of series with unbound singly charged anions since their $E(\lambda)$ would be parabolically tangent to the continuum edge at this point [$\lambda = (n-1)^{-1}$] owing to the long range Coulombic attraction in the cationic species.

In Sec. II we report variational calculations of the ionization energy $I(\lambda)$ for the ten-electron atomic ground state, for which physical values of λ represent Na^+, Ne, F^-, and O^{2-}. This sytem, discussed qualitatively in Ref. 2, was chosen because of the extra stability generally associated with a closed shell. The O^{2-} ion "ground state" is found to be unstable; we provide estimates of its energy and width. Our results indicate that recent determination of the O^- electron affinity by Cantor[11] from a Born–Haber cycle may require careful reinterpretation (Sec. III). In Sec. IV we discuss chemically relevant species for which stability of the dinegative ion ground state is most likely to be observed.

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II. IONIZATION POTENTIAL CALCULATIONS FOR THE O^{2-} SERIES

A. Wavefunction and Method

In order to calculate λ^* for a many-electron system we can invoke the nonlinear variational technique.[1-3] The trail wavefunction $\varphi(\boldsymbol{\alpha})$ must be flexible enough to describe at once both the localized n-electron bound state and the singly ionized $(n-1)$-electron state by an appropriate continuous transformation of the variational parameters $\boldsymbol{\alpha}$. Then λ^* is identified by following the ground-state minimum of the variational energy

$$E(\boldsymbol{\alpha}, \lambda) = \frac{\langle \varphi | \hat{H} | \varphi \rangle}{\langle \varphi | \varphi \rangle} \tag{1}$$

into the continuum as a function of λ until the point of instability is reached. This instability is located by diverging rates of change with respect to λ of the minimizing parameter values:

$$\left| \frac{\partial \alpha_j}{\partial \lambda} \right| = \infty , \tag{2}$$

where j labels components of the multidimensional parameter space. It is known[2] that the parametric instability creates a branch-point singularity in the variational energy with leading order $\frac{3}{2}$. For $\lambda > \lambda^*$ the stationary values of $E(\alpha, \lambda)$ may in principle be followed off the real energy axis by allowing the parameters to become complex.

For penetration of the ten-electron ground state into the $(1s^2 2s^2 2p^5)\ ^2P + e^-$ continuum the simplest wavefunction which allows a description of both the bound and ionized state is of the type

$$\varphi(\alpha) = \Phi + \alpha_0 \chi , \tag{3}$$

where Φ is a single determinatal function representing the $(1s^2 2s^2 2p^6)\ ^1S$ configuration, and χ is the fixed linear combination of $2p \to p'$ single excitation determinants giving the $(1s^2 2s^2 2p^5 p')\ ^1S$ configuration. This two-configuration function contains sufficient correlation to allow a single electron to be radially diffuse and eventually to ionize. Although higher order correlation effects are necessary for an accurate energy, the present function should suffice to give a reasonable estimate of λ^*. In particular, note that $\varphi(\boldsymbol{\alpha})$ does not introduce singularities in the variational energy associated with the direct double ionization of the ten-electron system.

The one-electron orbitals were taken to be products of radial orbitals times spherical harmonics and spin functions. Two simple linear combinations of Slater type orbitals were used for the radial basis. In set (A) we chose the functions

$$u_{1s} = N_{1s} \exp(-\alpha_1 r), \tag{4}$$

$$u_{2s} = N_{2s}[3 - (\alpha_1 + \alpha_2) r] \exp(-\alpha_2 r), \tag{5}$$

$$u_{2p} = N_{2p}\, r[\exp(-\alpha_3 r) + \alpha_4 \exp(-\alpha_3 r/2)], \tag{6}$$

where the N_{nl} are normalization factors. The ratio of exponents in u_{2p} was obtained from a partial optimization for F^-. Set (B) differed from (A) only by the use of a Hulthén type $2p$ radial function,

$$u_{2p} = N_{2p}[\exp(-\alpha_3 r) - \exp(-\alpha_4 r)]. \tag{7}$$

In both basis sets the one-electron radial correlation function $u_{p'}$ was approximated by the single term

$$u_{p'} = r^2 \exp(-\alpha_5 r) \tag{8}$$

orthogonalized to u_{2p}. Thus both calculations involved variation of six parameters. While the bases are admittedly crude, use of a limited set of parameters was advantageous since the calculations were repeated at many values of $\lambda > \frac{1}{8}$. In addition, near λ^* the energy function is very flat with respect to parameter variation in the neighborhood of the optimal $\boldsymbol{\alpha}$ values, and our basis assured a relatively fast and accurate convergence to the local energy minimum.

For $\lambda > \lambda^*$ the calculations are characterized by convergence of the (real) outer orbital exponent α_5 to zero, corresponding to the ionization of a single electron. For determination of the nine-electron ground state energy we therefore used a single determinantal wavefunction for the $(1s^2 2s^2 2p^5)\ ^2P$ configuration, with the parameters $\alpha_j (j = 1-4)$ reoptimized at each value of λ. The ionization potential $[\equiv I(\lambda)]$ was then taken as the difference between the nine- and ten-electron energies.

B. Numerical Results

The λ dependence of the calculated ten-electron ground state energy appears in Fig. 1. Note that the energies are scaled by λ^2 and are presented relative to the cal-

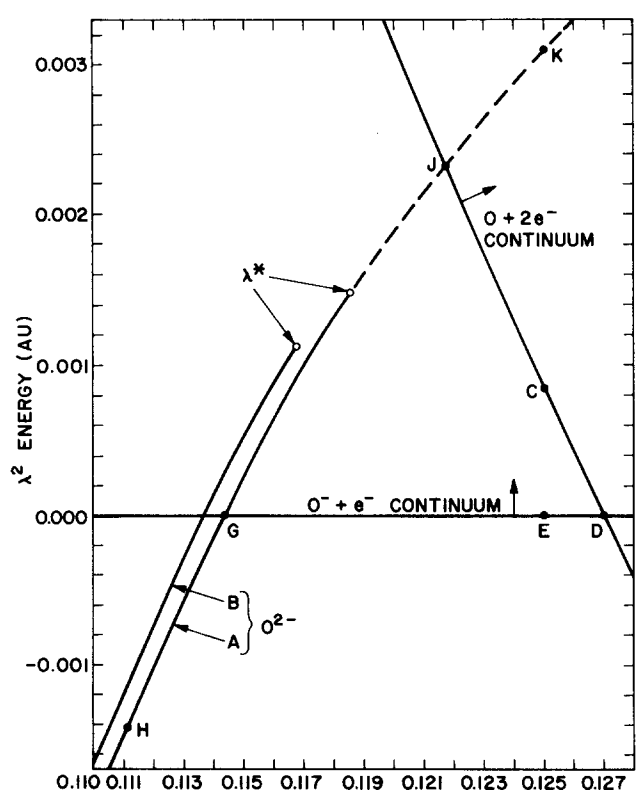

FIG. 1. λ-dependence of the ten-electron $^1S^e$ ground state variational energy minimum, and the doubly-ionized eight-electron $^3P^e$ ground state, relative to the singly-ionized nine-electron $^2P^0$ ground state energy. A complete description of this figure is given in Sec. II-B.

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culated first ionization threshold, so that the energies correspond to $-\lambda^2 I(\lambda)$. Curves A and B represent our variational calculations on the O^{2-} series using basis sets A and B, respectively. For instance, curve A rises through point H (the F^- anion at $\lambda=\frac{1}{9}$) and intersects the $O^- + e^-$ isoelectronic ionization continuum edge at $G(\lambda=\lambda_c)$. Beyond λ^*, the dashed line extension of A represents the real part of the complex energy (see Sec. II. C), with the location of the O^{2-} ion denoted by K. The second ionization threshold of the isoelectronic series is labeled "$O+2e^-$ Continuum", and intersects curve A at point J. This threshold was obtained simply by fitting the known ionization potentials of O^- (point C), F, and Ne^+[12,13] to a formula quadratic in λ. Point E represents the O^- ground state energy, and D is the intersection of the first and second ionization thresholds at $\lambda \cong 0.127$.

The calculated values of λ^* are

$$\lambda^*(A) = 0.11849$$

$$\lambda^*(B) = 0.1167,$$

which lie approximately halfway between the $F^-(\lambda=0.1\underline{1})$ and $O^{2-}(\lambda=0.125)$ anions. The intersection of the ground state with the first ionization continuum [i.e., $I(\lambda_c)=0$] occurs at

$$\lambda_c(A) = 0.1144$$

$$\lambda_c(B) = 0.1137.$$

The relative accuracies of the two calculations can be seen at F^-, for which the ionization energies are

$$I_A(\tfrac{1}{9}) = 3.118 \text{ eV},$$

$$I_B(\tfrac{1}{9}) = 2.523 \text{ eV}.$$

The observed ionization energy[14] is 3.448 eV. The value from calculation A is surprisingly good considering the limited flexibility of the radial basis set, but the agreement with experiment must be regarded as somewhat fortuitous. Nevertheless, the results suggest that estimates of the O^{2-} resonance energy made in the following section with basis set A may be reasonable. Additional physical ionization energies were calculated with basis set A for Ne(I = 20.60 eV) and Na^+(I = 45.96 eV), differing by 1 V from the observed values[12] 21.56 and 47.26 eV, respectively.

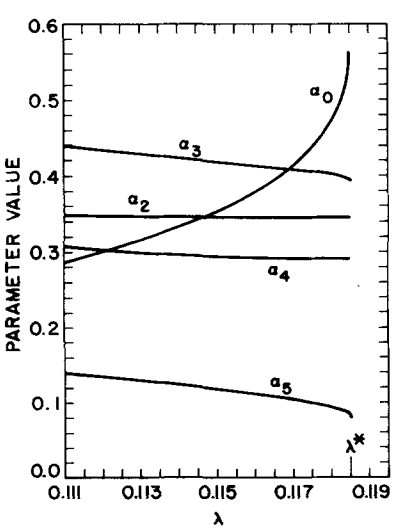

FIG. 2. λ-dependence of the optimal ten-electron trial wavefunction parameters for basis set A [Eqs. (3)–(8)]. The 1s orbital exponent (equal to α_1) is not shown, but varies nearly linearly with λ from 0.9670 (λ = 0.11) to 0.9653 ($\lambda=\lambda^*$).

No calculations were made with basis set B for $\lambda < \frac{1}{9}$, as the sole intent of this calculation was to ascertain the dependence of λ^* upon the 2p radial function. The difference in $\lambda^2 I(\lambda)$ between the two calculations as shown in Fig. 1 is nearly constant. Although calculation A gives a better ionization energy than B for F^-, it does not necessarily follow that $\lambda^*(A)$ is better than $\lambda^*(B)$ since the instability at λ^* is more sensitive than is the energy to the diffuse properties of the radial functions.

The λ dependence of the variation parameters for basis set A appears in Fig. 2. Note that only α_0 and α_5 show a marked instability at λ^* since they alone control the diffusivity of the outer orbital. The results for basis set B are qualitatively similar.

C. Estimate of O^{2-} Energy and Lifetime

The energy function $E(\lambda)$ has a branch cut along the positive λ axis, beginning at λ^* and stretching toward plus infinity. The values of $E(\lambda)$ along the cut are complex:

$$E = E_r \pm i\Gamma/2, \tag{9}$$

where the width Γ is taken to be nonnegative. If the existing helium-sequence calculations are typical,[1–4] then the imaginary part of the energy will be positive just above the cut and negative just below the cut. The latter case corresponds to a decaying state, with radially diverging current. The quantity Γ leads directly to the lifetime of the unstable species:

$$\tau = \hbar/\Gamma. \tag{10}$$

It also provides the resonance width for the unstable species formed spontaneously in a scattering experiment.

In a more complete numerical analysis than we have been able to undertake, the analytic function $E(\lambda)$ would be followed throughout the complex λ plane by identifying it with stationary values of the quantity $E(\boldsymbol{\alpha}, \lambda)$ in Eq. (1). For arbitrary complex λ, $E(\boldsymbol{\alpha}, \lambda)$ would have to be stationary with respect to variations of both real and imaginary parts of each parameter α_j.

We have in fact chosen to follow a simpler path. The existence of this path follows from the fact that $E(\boldsymbol{\alpha}, \lambda)$ can be expanded in a multiple Taylor series in the parameters $\boldsymbol{\alpha}$. The useful consequence, demonstrated by Stillinger and Weber,[2] is that near λ^* the stationary energy values have the form

$$\lambda^2 E(\lambda) = \lambda^2 E(\boldsymbol{\alpha}^*, \lambda) - k(\lambda^* - \lambda)^{3/2} + O[(\lambda^* - \lambda)^2]. \tag{11}$$

In this expression $\boldsymbol{\alpha}^*$ is the parameter set that causes $E(\boldsymbol{\alpha}, \lambda^*)$ to be stationary. If λ is reasonably close to λ^*, the two terms explicitly shown in Eq. (11) should alone provide an adequate approximation. In particular we shall attribute the width Γ for O^{2-} entirely to the $\frac{3}{2}$ power term, with the value of k in Eq. (11) extracted from real energy calculations for λ slightly less than

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λ^*. The corresponding width for O^{2-} is obtained from the imaginary part of Eq. (11) at $\lambda = \frac{1}{8}$, the result being (in atomic units)

$$\Gamma(O^{2-}) = \lim_{\lambda \to \lambda^* - 0} \Delta(\lambda) \left(\frac{(\frac{1}{8}) - \lambda^*}{\lambda^* - \lambda} \right)^{3/2}, \tag{12}$$

where

$$\Delta(\lambda) = 128\lambda^2 [E(\alpha^*, \lambda) - E(\lambda)]. \tag{13}$$

Using numerical results for basis set A, we find that $\Gamma(O^{2-})$ is 1.3 eV. The corresponding lifetime of the unstable O^{2-} state is short, 5.0×10^{-16} sec. It is possible that this broad resonance would be observed in $e^- + O^-$ elastic scattering, corresponding to temporary formation of O^{2-}. The preceding estimated lifetime is too short to account for the reported O^{2-} ion resulting from a Penning discharge,[15] which may therefore correspond to a different electronic state.

The position of the O^{2-} resonance is controlled by the real part of $I(\lambda)$ evaluated at $\lambda = \frac{1}{8}$. By using the fitting formula

$$\lambda^2 I(\lambda) = a_0 + a_1(\lambda^* - \lambda) + a_2(\lambda^* - \lambda)^{3/2} + a_3(\lambda^* - \lambda)^2 \tag{14}$$

in a least-squares analysis of A-basis calculations (to fix $a_0 \cdots a_3$), we find that

$$I_r(O^{2-}) \cong -5.38 \text{ eV}. \tag{15}$$

This negative electron affinity should represent the incident electron kinetic energy in $e^- + O^-$ scattering at the middle of the broad O^{2-} resonance.

A variety of ionization potential formulas have been proposed, from which it is possible by extrapolation to infer values for at least singly charged anions. However these formulas do not account for development of widths, so their extension to dinegative anions involves considerable uncertainty, One example, for ten electrons, is Edlén's three-parameter formula[12]; when applied to O^{2-} it predicts -5.31 eV for I_r which agrees favorably with our own value. However, analogous formulas proposed by Kaufman,[16] using two and three parameters, give -7.17 eV and -6.53 eV, respectively, for $I_r(O^{2-})$. We also note in passing that a simple quadratic fit in λ to experimental $\lambda^2 I(\lambda)$ values for F^-, Ne, Na^+ implies that $I_r(O^{2-}) = -7.09$ eV. Since this class of $I_r(\lambda)$ formulas fails to account for a branch-point singularity, and in particular fails to include infinite negative curvature there, it is not surprising that implied results for $I_r(O^{2-})$ scatter widely.

Our O^{2-} ionization energy is more positive than the value -6.04 eV calculated by Clementi and McLean[17] using the Hartree–Fock approximation augmented by a rough correlation correction. Numerical convergence of their O^{2-} ground state is doubtful, however, due to occurrence of a positive $2p$ orbital energy. No bound O^{2-} state was found in the self-consistent-field calculations of Roothaan and Kelly.[18]

We emphasize that our estimates of the energy included only the leading-order singularity at λ^*, with index $\frac{3}{2}$. Future investigations of O^{2-} should employ extensive multiconfiguration calculations to determine λ^* more accurately and to characterize the singularity in greater detail. Such calculations would also allow determination of the partial width for the two-electron detachment

$$O^{2-} \to O + 2e^-,$$

which is energetically allowed but not described by our present wavefunctions.

III. COMPARISON WITH THERMODYNAMIC OXYGEN AFFINITY

The Born–Haber cycle[19] has often been used to estimate anion electron affinities. In particular, Cantor[11] has recently used this approach to calculate $I(O^{2-})$ from thermodynamic data on oxides of divalent metals. Stripped down to its essentials, the Born–Haber cycle applied to these oxides is illustrated in Fig. 3. In that diagram the following symbols have been used:

I, I' are the ionization potentials of O^{2-}, O^-, respectively; A, A' are the electron affinities of M^+, M, respectively; S is the sublimation energy of gaseous M to its crystalline form at 0 °K; D is the ground-state dissociation energy of O_2; Q is the heat of reaction (at 0 °K) of M(c) and O_2(g) to form MO(c); $U(R)$ is the lattice energy of MO(c) for the nearest-neighbor spacing R(R_c is the equilibrium crystal spacing).

Traversing the entire cycle must lead to zero net change in energy, so one has

$$I(O^{2-}) = U(\infty) - U(R_c) + A - I' + A' - S + \tfrac{1}{2}D - Q. \tag{16}$$

The crystal energy $U(R)$ is constructed from electrostatic Madelung energy, plus short range interactions estimated from elastic properties (usually) and the requirement that U exhibit a minimum at R_c. Unlike the more favorable situation that obtains for alkali halides, precise definition of $U(R)$ for oxide crystals is hampered by two conceptual difficulties.

(1) As R increase from R_c, it would become energetically favorable for electrons to tunnel from the O^{2-} anions to the M^{2+} cations to form O^- and M^+. This apparently implies an avoided crossing between the $U(R)$ curve and its hypothetical analog for $M^+ + O^-$.

(2) Our calculations show that O^{2-} is *not* a stable species in isolation, as required in the upper right hand corner of Fig. 3.

Without accounting for these conceptual difficulties, Cantor has calculated that

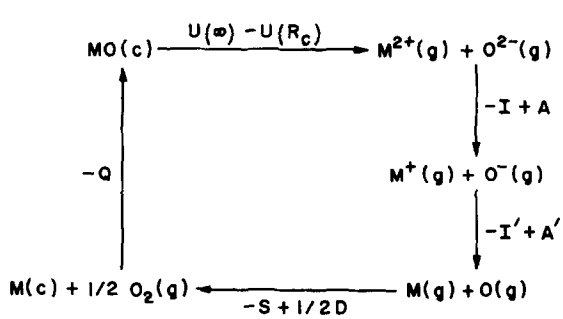

FIG. 3. Born–Haber cycle for metal oxides, as discussed in Sec. III.

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$$I(O^{2-}) = -7.93 \pm 0.35 \text{ eV}. \tag{17}$$

The error limits were assigned on the basis of apparent imprecision of the energies in the Born-Habor cycle as postulated. However (1) and (2) above clearly introduce extra uncertainties, so it is not clear that Cantor's result (17) seriously contradicts or discounts our own estimate, -5.38 eV.

A formal (though probably impractical) way to circumvent difficulties (1) and (2) would be to use an extra attractive potential $V(r)$ to stablize O^{2-}. The nuclear potential at each oxygen, normally $-8e^2/r$, could in principle be modified to

$$-8e^2/r + \xi V(r), \tag{18}$$

where ξ is to be "turned on" adiabatically from zero to unity. $V(r)$ could be a broad square well, for example; its role is simply to depress the energy of O^{2-} to prevent spontaneous electron loss and to prevent near curve crossing.

The Born–Haber cycle would thereupon become somewhat more complex, as Fig. 4 shows. As ξ increases from 0 to 1 in the MO crystal, the energy changes by Δ_1. On account of the V's attached to each oxygen, the lattice energy versus separation R will be modified from the previous function $U(R)$, to $U_V(R)$, possibly with a shifted minimum position R_{cV}. The ionization potential of O^{2-} in the presence of V has been denoted by I_V. If ξ is reduced from 1 to 0 for the initially stabilized free O^{2-}, a complex energy change Δ_2 arises since the end product has a finite lifetime; we require only its real part, as shown in Fig. 4.

Combining terms from Fig. 4, we see that the formal ionization potential of free unstabilized O^{2-} must be

$$\begin{aligned} I(O^{2-}) &= I_V - \mathrm{Re}(\Delta_2) \\ &= U_V(\infty) - U_V(R_{cV}) + A - I' + A' - S + \tfrac{1}{2}D - Q - \mathrm{Re}(\Delta_2). \end{aligned} \tag{19}$$

In order for Eq. (16) to yield the correct result, it is necessary that

$$U(\infty) - U(R_C) = U_V(\infty) - U_V(R_{cV}) - \mathrm{Re}(\Delta_2). \tag{20}$$

It seems to require an unlikely coincidence to have this identity fulfilled.

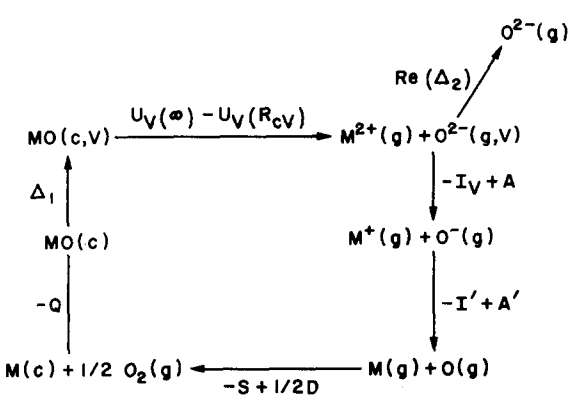

FIG. 4. Modified Born–Haber cycle which allows for the instability of O^{2-}, as discussed in Sec. III.

We suggest that quantum-mechanical calculations alone should be given primary emphasis for estimating energies of unstable free anions.

IV. APPLICATION TO OTHER DINEGATIVE IONS

The method used in Sec. II for calculating the O^{2-} energy and width may be applied equally well to the λ variation energy of other first row isoelectronic series which include bound monovalent anions (e.g., C^- and O^-), provided that the trail wavefunction is sufficiently flexible. It is unlikely, however, for the ground state configurations that the corresponding dinegative ions would be more stable than O^{2-}. The situation may well be different for larger atomic systems, and a likely candidate for a relatively stable dinegative ground state would be the 18-electron anion S^{2-}, which is isoelectronic with Ar. An estimate of λ^* for the S^{2-} ground state energy follows upon noting that the 2-, 10-, and 18-electron systems in the region $\lambda \cong \lambda^*$ can be described be wavefunctions of a similar type, namely one radially diffuse electron excited from a closed shell [cf. Eq. (3)]. The effective charge seen asymptotically by the outer electron is $(Z - N + 1)$, N being the total number of electrons. It is therefore plausible that the degree of stability of the binding energy near λ^* should be similar for different anions in which $\Lambda_N = \lambda(N-1)$ is the same. For instance in calculation (A) $\Lambda_{10} = 1.07$, while for the 2-electron system a similar computation[1] gives $\Lambda_2^* = 1.08$. A greater stability would then be expected for the S^{2-} ion ($\Lambda_{18} = 1.0625$) than for O^{2-} ($\Lambda_{10} = 1.125$), assuming that $\Lambda_{18}^* \cong 1.07$. In fact this estimate suggests that there may be a much narrower resonance in the $e^- + S^-$ scattering cross section than was predicted for the O^{2-} resonance. Stability in the S^{2-} ion—either observed or computed—would mean that the method of determining energies and widths used in the present paper could be usefully extended to even higher charged anions, as in the series

Ar, Cl^-, S^{2-}, P^{3-};

Kr, Br^-, Se^{2-}, As^{3-};

Xe, I^-, Te^{2-}, Sb^{3-}.

A knowledge of these energies would be important in understanding crystal lattice energies.

The possibility that bound dinegative ions exist either below or above the continuum edge is more likely for molecules than for atoms owing to the relative sizes of the systems. While little is known generally about the stability of isolated dinegative molecular ions, there is evidence for their existence in the gas phase formation of a doubly charged benzo[*cd*]pyrene-6-one dimer.[20]

Computation of accurate energies as a function of λ, and the concurrent determination of λ^* is not practical for large molecules. For small molecules, and in particular diatomic isoelectronic series such as $\cdots N_2$, C_2^{2-}, the λ variation method would be useful for predicting dinegative ion stabilities. An alternative to the full λ variation, where λ is the inverse of the total nuclear charge, would be to vary the charge at only a portion of the atomic centers. A case in point is the isoelectronic series ClO_4^-, SO_4^{2-}, PO_4^{3-}.[21]

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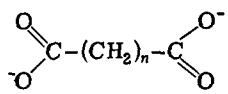
In addition to studying the effects of variable nuclear charge, it will also be revealing to determine the influence of nuclear geometry on anion stability. One of the simplest such investigations would involve the potential energy curve of $H^- + H^-$ and would be to see at what distance (in comparison with the $H + H^-$ curve) one of the four electrons spontaneously autoionizes. An analogous case concerns the homologous sequence of dicarboxylic acid anions ($n = 0, 1, 2 \cdots$):



As n decreases, electrostatic repulsion should destabilize the dianions. It would be valuable to learn the n range leading to autoionization, and to know if any values of n lead to stable states in the ionization continuum.

V. CONCLUSION

We have demonstrated a method which allows direct calculation of energies and lifetimes of dinegative ion states which lie in the first ionization continuum. A key feature of the method is that nonlinear bound state variational energies are analytically continued around a branch point singularity as $1/Z$ is continuously scaled. Results were presented for the O^{2-} ion which may have important consequences for the determination of crystal lattice energies and for the measurement of $O^- + e^-$ scattering cross sections. Several dinegative ions were mentioned as examples of bound states or narrow resonances in a continuum of the same symmetry. The verification of (a) the accuracy of the present method and (b) the existence of a real (i.e., physical) continuum bound state awaits further theoretical and experimental investigation of the anions discussed.

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