

Isolated-core excitations in strong electric fields. I. Theory

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A basic theory is presented for the photoexcitation of a core state of a Rydberg atom in any type of static field; in this situation, the core state is excited by the photon while the Rydberg electron is essentially a spectator. This simple picture is made interesting through the interaction of the Rydberg electron with the core which can cause a change in the Rydberg electron's state and can cause the Rydberg electron to autoionize. The method is computationally efficient and has been used for alkaline-earth atoms in a static electric field. An approximation to the formalism is presented that illustrates a mechanism controlling the isolated core excitation in a static electric field; this approximation may serve as a paradigm for extending the interpretation of isolated core spectra to other types of fields.

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I. INTRODUCTION

There are many tools that have been used to probe correlation in many electron atoms. The study of photoabsorption spectra is especially useful since the high resolution of the laser allows precise determination of the energies and widths of the states while the strength of transitions contains information about the composition of the state. Most photoabsorption studies use compact initial states which thus probe final-state correlation as manifested near the nucleus. By contrast, the technique known as isolated core excitation utilizes a highly excited initial state [1–8]. With this technique, the atom is initially prepared such that one electron is excited to a Rydberg state with the remaining electrons left in the ground state of the positive ion. A second laser is then scanned over optically allowed transitions of the positive ion. A large ionization signal is observed at the frequencies of optically allowed transitions in the core; ionization is also observed at other frequencies because both the core and the Rydberg electron can simultaneously make transitions due to the electron-core interaction.

The isolated core excitation directly probes the interaction of the Rydberg electron with the core electrons. In the excitation process, the core changes character which thus changes the potential for the Rydberg electron. The strength of the excitation to the final state depends almost solely on the projection of the initial Rydberg wave function onto the final Rydberg wave function. If the potential for the Rydberg electron is unchanged, then only one final state is excited. As the change in the potential increases, then the character of the final states change and increasingly many final states can be excited. The electron-core interaction is also manifested through the autoionization widths of the final states. Often, the resonance widths can be measured quite simply using isolated core excitations because there is very little direct excitation to the open channels. Thus, there is little interference between the direct ionization path and the indirect ionization path through the resonance states; the photoabsorption cross section near a resonance is often a simple Lorentzian.

In the past, most isolated core experiments and all isolated core calculations were for atoms unperturbed by static fields.

Two previous studies presented experimental results for isolated core excitations by a cw laser for Mg in a static electric field [6] and by a pulsed laser for Mg in a static electric field [7]. It is important to extend the study of isolated core excitations to atoms in strong, static fields. Photoionization by isolated core excitations is the time reverse of dielectronic recombination (DR). In DR, an electron scatters from an ion, excites the ion so that it is captured into a doubly excited resonance state, and is stabilized when the core electrons emit a photon. It is known that static electric fields (for example, the microfields that exist in plasmas) can affect the recombination rate due to the l mixing of the autoionizing Rydberg states [9,10]. Early measurements [11] and calculations [12] showed the effect of electric fields on a Rydberg series. However, it has not yet been possible to perform detailed comparisons between experimental and calculated recombination cross sections for individual resonances in a static electric field; this is because the resolution in electron scattering experiments is not high enough to resolve the Rydberg states that are most strongly affected. The isolated core excitations can be studied with high resolution since the limitation is from the resolution of a laser. Thus, detailed comparison can be performed at the individual resonance level.

Finally, it is also worth studying isolated core excitations in static electric fields as an interesting example of channel interactions and correlations between different degrees of freedom. The Hamiltonian for the nonrelativistic treatment of a hydrogen atom in a static electric field separates in parabolic coordinates. However, the Hamiltonian does not separate for any other atom in a static electric field. For a Rydberg state with an excited ion core, the electron-electron interactions can cause the Rydberg electron to scatter between different channels in parabolic coordinates while keeping its total energy fixed; also, this interaction can cause an exchange of energy between the Rydberg electron and the ion which may lead to the ejection of an electron from the atom. The competition and interplay between these two types of correlation can give interesting features in the spectra. In the isolated core excitation, the initial state is already a Rydberg state and can be chosen to be a state that is essentially an uncoupled state in parabolic coordinates or a state that is essentially an angular momentum eigenstate; this leads to a

level of control over what aspects of the final states are probed.

Although no specific results are presented for isolated core excitations in a static magnetic field and no experiments have yet been performed, it may be that this will be the most interesting case. Classically, the motion of an electron in a Coulomb potential plus static magnetic field can be either regular or chaotic depending on the scaled energy whereas the motion can only be regular in a static electric field. There are several fascinating features of an electron's eigenstates in a Coulomb potential plus static magnetic field, including the scarring of the wave function on the unstable classical trajectories. How will the isolated core spectra reflect these features? Will the number of final resonance states that are excited in an isolated core excitation increase or decrease when going from the classically regular region to the classically chaotic region?

In this and the following two papers [13,14], the properties of isolated core excitations in static electric fields are studied. In this paper a basic theory for isolated core excitations in static fields will be presented; some of the implications of the theory will be discussed. In the second paper [13], the experimental results for isolated core excitations in Mg will be compared to the theory; the relationship of this data with previous time-resolved electron-emission measurements [7] and some of the interesting properties of Mg will be discussed. In the third paper [14], the experimental results for isolated core excitations in Ba will be compared to the theory; some of the interesting properties of Ba isolated core excitations will be discussed. Atomic units will be used throughout this paper.

II. THEORY OF ISOLATED CORE EXCITATIONS IN STATIC FIELDS

In this section I give a derivation of a method for calculating dipole matrix elements for isolated core excitations (ICE) in static fields. This derivation is later recast into an approximate form that more clearly shows the mechanisms controlling the cross section for ICE in an electric field. A derivation of the isolated core dipole matrix elements in zero field is given in the Appendix to enable a comparison between the treatment in this paper and the older formalism.

A. ICE in a static field

The starting point for ICE theory is the idea that it is the core electrons that absorb the photon while the Rydberg electron is a spectator. This is a good approximation because the photon-absorption process happens most efficiently when an electron is near the core; the core electrons are localized near the nucleus whereas the Rydberg electron has only a small probability to be found in this region.

To apply the theory, it is assumed that the static field is too weak to perturb the electrons when they are near the core (outside of an overall energy shift); as a conservative estimate, the fields should be weaker than 10^{-3} atomic units. This condition is satisfied by even the strongest laboratory strength fields available today. It is thus possible to separate the wave function into an inner and outer region. In the inner

region, the wave function can be represented as a superposition of zero-field wave functions. In the outer region, the field can drastically change the wave function from its zero-field form. For convenience, I will represent the wave function near the core using multichannel quantum-defect theory, although this restriction can be easily removed. For example, the formalism can be easily extended to compute dipole matrix elements when the wave function is obtained from R -matrix calculations.

The main difficulty is in obtaining the dipole matrix elements between the initial bound state α and the final continuum states β ; it is assumed that the problem of computing the wave function in the field is solved. This dipole matrix element will be denoted $d_{\beta\alpha} = \langle \Psi_\beta | D | \Psi_\alpha \rangle$. The i th core state will be denoted by the symbol Φ_i ; the core state will also include the spin of the Rydberg electron in order for the wave function of the Rydberg electron to only depend on the spatial coordinates. The energy of the core state will be given by E_i . The symbol i actually denotes several properties of the core state: $\chi_i J_{c,i} Q_i \mu_i$ where the parameter χ_i denotes all of the quantum numbers of the core *except* the total angular momentum, $J_{c,i}$ is the total angular momentum of the i th core state, Q_i is the angular momentum that results from coupling the angular momentum of the core to the spin of the Rydberg electron, and μ_i is the eigenvalue of the projection of the Q_i angular momentum on the z axis. As an example from Mg, the χ_8 is the $1s^2 2s^2 2p^6 3p$ state of Mg^+ , $J_{c,8} = 3/2$, $Q_8 = 2$, and $\mu_8 = -1$.

The initial and final wave functions can be quite complicated due to the channel couplings that arise from the electron-electron interactions near the core. The α th initial state can be represented as

$$\Psi_\alpha = \sum_i \Phi_i A_{i\alpha}(\mathbf{r}) \text{ for } |\mathbf{r}| > r_c, \quad (1)$$

where the cutoff radius r_c is typically less than 10 a.u. Since the Rydberg electron is outside of the core region for this part of the wave function, the Rydberg wave function is a solution of a one-electron Hamiltonian with a potential that is simply the Coulomb potential plus the potential from the field, $H_F A_{i\alpha} = \epsilon_{i\alpha} A_{i\alpha}$; the energy of the Rydberg electron will be given by $\epsilon_{i\alpha}$ such that the energy of the α initial state is $E_\alpha = E_i + \epsilon_{i\alpha}$. The $A_{i\alpha}$ go to zero or effectively go to zero [15] as $|\mathbf{r}| \rightarrow \infty$. The β th continuum function can be written in a similar form

$$\Psi_\beta = \sum_i \Phi_i B_{i\beta}(\mathbf{r}) \text{ for } |\mathbf{r}| > r_c. \quad (2)$$

Again, the Rydberg wave function is a solution of a one-electron Hamiltonian with a potential that is simply the Coulomb potential plus the potential from the field, $H_F B_{i\beta} = \epsilon_{i\beta} B_{i\beta}$; the energy of the final state is $E = E_\alpha + \omega = E_i + \epsilon_{i\beta}$ where ω is the photon energy.

The dipole matrix elements may be obtained to a good approximation by noting that the photon is absorbed by the core electrons and that the spatial extent of the Rydberg electron is large compared to the core,

$$d_{\beta\alpha} = \sum_{ii'} D_{ii'} \int B_{i\beta}^*(\mathbf{r}) A_{i'\alpha}(\mathbf{r}) dV \quad (3)$$

[compare to Eq. (A3)] where the integration for the Rydberg wave function extends over all space outside of the core region and the core dipole matrix elements are $D_{ii'} = \langle \Phi_i | D | \Phi_{i'} \rangle$. The approximations in this equation are that the effect from the dipole operator on the Rydberg electron is not included and the projection of A onto B is only for the region outside of the core. The error in the dipole matrix element from each of these approximations will be proportional to $1/n^{3/2}$ where n is the principle quantum number of the initial state and thus the error in the cross section will be quite small for Rydberg states.

The relationship of the product B^*A to the Wronskian [16] of B^* and A can be substituted into the equation for the dipole matrix element, Eq. (3), to obtain a surface integrals at the radius $|\mathbf{r}| = r_c$ and a surface integral at $|\mathbf{r}| \rightarrow \infty$. The latter surface integral is zero since the original bound-state function goes to zero at large distances. This leaves the surface integral at the cutoff radius

$$d_{\beta\alpha} = \frac{r_c^2}{2} \sum_{ii'} D_{ii'} \int W(A_{i'\alpha}, B_{i\beta}^*) d\Omega / (\epsilon_{i\beta} - \epsilon_{i'\alpha}), \quad (4)$$

where the integration is only over the angles $d\Omega = d\varphi d\cos\theta$ and the radial Wronskian $W(A, B^*) = (\partial B^*/\partial r)A - B^*(\partial A/\partial r)$ is evaluated at r_c . This expression is general and only entails knowing the Rydberg wave functions at a radial surface close to the core. These surface integrals may be obtained from many different types of calculations including R matrix [17] or multichannel quantum-defect theory (MQDT) [18,19]. Equation (4) is the main result of this paper; the rest of this section and the following sections are only devoted to discussing methods of implementation and to discussing some of the implications of this equation. Of course, this equation also applies when there is no field present, in which case it reduces to the usual expression for ICE dipole matrix elements.

B. MQDT form of dipole matrix elements

As an illustration, specific formulas for the dipole matrix element will be obtained in terms of the MQDT parameters. Near the core the wave functions are not affected by the field and thus may be represented in terms of the zero-field functions. I will choose to utilize the K -matrix form of the functions at small distances. For the bound state, these functions are

$$\psi_{i'}^{(0)} = \sum_i \Phi_i Y_{l_i m_i}(\Omega) [f_i(r) \delta_{ii'} - g_i(r) K_{ii'}^{(0)}] / r \quad (5)$$

[compare to Eq. (A6)] where Y_{lm} is the spherical harmonic, the f, g are field-free regular and irregular Coulomb functions, and $K^{(0)}$ is the K matrix at the energy of the bound state. For the final state, these functions are

$$\psi_{i'}^{(f)} = \sum_i \Phi_i Y_{l_i m_i}(\Omega) [f_i(r) \delta_{ii'} - g_i(r) K_{ii'}^{(f)}] / r \quad (6)$$

[compare to Eq. (A7)] where $K^{(f)}$ is the K matrix at the energy of the final state. The initial-state function and final-state function near the core are superpositions of these functions,

$$\Psi_\alpha = \sum_i \psi_i^{(0)} \zeta_{i\alpha}^{(0)} \quad \text{and} \quad \Psi_\beta = \sum_i \psi_i^{(f)} \zeta_{i\beta}^{(f)}. \quad (7)$$

Using these formulas and the Wronskians [20] for the Coulomb functions, the dipole matrix elements may be obtained in terms of the K matrices, core dipole matrix elements, and the transformation coefficients to obtain the α initial state and the β final state,

$$d_{\beta\alpha} = \frac{1}{\pi} \sum_{i,i'} [D_{ii'} \delta_{l_i l_{i'}} \delta_{m_i m_{i'}} / (\epsilon_{i\beta} - \epsilon_{i'\alpha})] \times \sum_{i''} [\zeta_{i\beta}^{(f)*} K_{i'i''}^{(0)} \zeta_{i''\alpha}^{(0)} - K_{ii''}^{(f)} \zeta_{i''\beta}^{(f)*} \zeta_{i'\alpha}^{(0)}] \quad (8)$$

[compare to Eq. (A8)]. The accuracy of these expressions is directly related to the accuracy of the short-range scattering parameters (i.e., the K matrices) and the accuracy of the transformation parameters that give the states in the field in terms of the field-free states near the core (i.e., the ζ vectors). I expect that the approximations used to derive these formulas are much more accurate than the approximations that are used to obtain the scattering and transformation parameters. One of the more interesting features of this derivation is that the field dependence only enters through the transformation coefficients. Whether the atom is in a static electric field or magnetic field or a combination of the two is not important for the form of the matrix element.

There is a peculiar feature of Eq. (8); because K matrices decrease rapidly with l for l larger than 2 or 3, Eq. (8) apparently shows that only the low- l part of the Rydberg wave function contributes to the dipole matrix element. This is quite surprising because a Rydberg state of energy ϵ often contains a large number (roughly $1/\sqrt{-2\epsilon}$) of l components. It is apparently a paradox or error that the overlap of two Rydberg states (where both can have a large range of l components) is determined only by the low- l part of the states. Actually, the high- l part of the Rydberg wave functions do contribute substantially to the overlap. This contribution is hidden in the transformation coefficients ζ ; the high- l part of the wave function strongly affects the energy dependence of the transformation coefficients which, with the K matrices, determine the dipole matrix elements.

C. Approximation for a static electric field

The equations from the preceding section are expected to be very accurate when the atomic scattering and transformation parameters can be computed accurately. In all of the calculations presented in the following papers, the results from the preceding section are used. However, it is impos-

sible to gain an intuitive understanding from the preceding section due to the generality of the derivation. This section is devoted to deriving and discussing an approximation to the ICE dipole matrix element in a static electric field that more clearly shows the mechanisms controlling ICE in a field. The ideas for the form of an electric field, multichannel wave function are from Ref. [18] which is based on Ref. [19].

The idea is to do the opposite of the derivation in the preceding section where we superposed zero-field atomic wave functions; this resulted in a formulation in terms of zero-field parameters and transformation coefficients that include the field effects. Here we will superpose the solutions in the field that have the correct asymptotic boundary conditions; the coefficients of the superposition are determined by forcing the wave function with the correct boundary condition in the field to match onto the correct atomic wave function at short distances.

The Hamiltonian for an electron in a Coulomb potential plus static electric field is separable in parabolic coordinates. The wave functions can be written as superpositions of the solutions in parabolic coordinates in the form

$$B_{i\beta}(\mathbf{r}) = \sum_{n_1 m} F_{\epsilon_{i\beta} n_1 m}(\eta) \Xi_{\epsilon_{i\beta} n_1 m}(\xi, \phi) Y_{n_1 m, \beta}^{(0)}, \quad (9)$$

$$A_{i\alpha}(\mathbf{r}) = \sum_{n_1 m} F_{\epsilon_{i\alpha} n_1 m}(\eta) \Xi_{\epsilon_{i\alpha} n_1 m}(\xi, \phi) Y_{n_1 m, \alpha}^{(f)},$$

where Y are the transformation coefficients that give the correct match to the atomic wave function near the nucleus, the functions Ξ are bounded functions and play the role that the spherical harmonics play in spherical coordinates (the number of nodes in the ξ direction is n_1), and the F functions go to zero as η gets large when the channels are strongly closed. The F functions vary rapidly with energy near the origin and it is useful to express this function in terms of parameters that vary rapidly with energy and functions that vary more slowly. This combination is $F_{\epsilon n_1 m} = f_{\epsilon n_1 m} \cos[\delta_{n_1 m}(\epsilon)] + g_{\epsilon n_1 m} \sin[\delta_{n_1 m}(\epsilon)]$ where $\delta_{n_1 m}(\epsilon)$ is roughly the WKB phase accumulated in the η direction for channel n_1, m ; in zero field the phase accumulated in the channel is $\delta = \pi\nu = \pi/\sqrt{-2\epsilon}$. Compare this equation to Eqs. (A1) and (A2). The f, g functions are chosen to have the same Wronskians as the zero field case.

We can use these functions in the dipole formula but instead of choosing a spherical surface we can choose a surface of small η . This gives an approximate expression for the dipole matrix element as

$$d_{\beta\alpha} \approx \frac{1}{\pi} \sum_{i, i'} D_{ii'} \sum_{n_1 m} Y_{n_1 m, \beta}^{(0)} Y_{n_1 m, \alpha}^{(f)*} \times \frac{\sin[\delta_{n_1 m}(\epsilon_{i\beta}) - \delta_{n_1 m}(\epsilon_{i'\alpha})]}{(\epsilon_{i\beta} - \epsilon_{i'\alpha})} \quad (10)$$

[compare to Eq. (A5)]. The main reason that a \approx symbol is used in this equation is that another level of approximation has been utilized which is not as high in accuracy as the

previous approximations. In this approximation the Ξ functions have been treated as orthonormal over the surface even when $\epsilon_{i\beta} \neq \epsilon_{i'\alpha}$; these functions are only orthonormal when evaluated at the same energy. Equation (10) has not been used in the numerical calculations where high accuracy is desired but it is useful for interpreting the expected behavior of ICE in static electric fields.

It is interesting to note that the field-dependent properties are explicit in Eq. (10) but the parameters that specify the atom, the short-range scattering matrices, are only included implicitly through the transformation matrices Y . For the derivation in the preceding section, the atomic scattering parameters were explicit but the parameters that specify the type of field and the field strength are only included implicitly through the transformation matrices ζ . It is uncertain which form will be more useful for future calculations and experiments. For example, it might be possible to extend the Eq. (10) to other types of fields. The phase δ is approximately equal to the phase accumulated by the electron in traveling from small to large η . Perhaps for ICE in other static fields for which a separation of variables is not possible, this formula will still hold but with the phase differences calculated semiclassically.

III. DISCUSSION

I expect Eq. (10) to be accurate except for transitions so far off resonance that the principle quantum number changes. The equation will still be qualitatively accurate in this case; however, the accuracy decreases as the change in the n -manifold increases. Therefore, I will only examine the implications for transitions where the core is excited and the Rydberg electron also changes quantum numbers but within its original n manifold. When the change in energy is less than $1/n^3$ (the requirement for not changing the n manifold of the Rydberg electron), the phase difference $\delta_{n_1 m}(\epsilon_{i\beta}) - \delta_{n_1 m}(\epsilon_{i'\alpha})$ is less than π and can be approximated by $(\epsilon_{i\beta} - \epsilon_{i'\alpha}) d\delta_{n_1 m}/d\epsilon$ plus higher-order terms in the energy difference. This means that the leading energy-dependent term in the second line of Eq. (10) is the slowly varying function $d\delta_{n_1 m}/d\epsilon$.

To get a better idea of the general features of the ICE spectrum, it is necessary to have at least a crude understanding of the behavior of the transformation coefficients Y . There are two extreme cases that will be considered for the initial state. The first is when the initial state is not changed strongly by the static field. For example, a small- l Rydberg state will not mix with the other l components of the n manifold until a large enough field strength is used. In this case, the $Y^{(0)}$ coefficients are substantial for a large number of channels n_1 ; the precise distribution depends on whether the low- l state has mainly $s, p,$ or d character. The second extreme case is when taking a state with strong- l mixing from the field. In this case, the $Y^{(0)}$ coefficients are substantial only for a small fraction of the allowed channels, n_1 .

The properties of the final-state transformation coefficients are more difficult to understand. In the final state, there are many resonances ρ with perhaps wildly differing

energies ϵ_ρ and widths Γ_ρ . Roughly, the form of the coefficients is given by

$$Y_{n_1 m \alpha}^{(f)} \sim \sum_\rho U_{n_1 m, \rho} C_{\rho \alpha} / (\epsilon_{i\alpha} - \epsilon_\rho + i\Gamma_\rho/2), \quad (11)$$

where the parameter $U_{n_1 m, \rho}$ gives the fraction of the ρ resonance with character in the n_1, m channel and the parameter $C_{\rho \alpha}$ gives the fraction of the ρ resonance in the final state α . Again, there are two extreme cases that will be considered. If the angular momentum of the resonance is dominated by one low- l channel, then the $U_{n_1 m, \rho}$ will be distributed over many n_1 channels; these resonances tend to be relatively broad because the Rydberg electron can easily reach the core electrons and scatter into the open channels. However, if the state is strongly mixed by the field then the U coefficients are substantial only for a small fraction of the allowed channels n_1 ; these resonances tend to be relatively sharp because the Rydberg electron has a substantial amount of high- l character and thus does not strongly interact with the core electrons.

We can combine the ideas of this section to note that a resonance ρ in the final state will be excited with an amplitude proportional to $\sum_{n_1 m} Y_{n_1 m, \beta}^{(0)} U_{n_1 m, \rho}$. First consider the case when the initial state has not strongly mixed with other l states. The spectrum will have two types of structures from the final states: sharp features from the field mixed states and broader features from the unmixed final states. The proportion of each type of feature will depend on the strength of the mixing in the final state. If the field is too weak to cause the initial- l to mix in the final state, then only relatively broad features like in zero-field spectra will be visible. However, if the field is strong enough to cause mixing in the final state, then mostly sharp features related to the Stark states will be seen; there will be a large number of these sharp features that will be visible because each of the final Stark states have some low- l character. Perhaps surprisingly, it will not be difficult to find cases where the l state is not mixed in the initial state but is mixed in the final state. The field strength needed to cause mixing depends on the difference of quantum defects with l ; these differences can be substantially different for the initial and final states.

Now consider the case when the initial state is a strong mixture of l states so that the $Y_{n_1 m, \beta}^{(0)}$ is substantial for only a few n_1 . In this case, the spectrum will only show features in a small energy range near the ionic transitions. Very few resonances ρ will be substantially excited and these will be the sharp resonances that have a strong l mixing with a similar character to the initial state. An exception is when states from a different threshold fall very near the energy of the unperturbed final states and mix with them through configuration interaction; in this case, there will be several states that have a large fraction of their character the same as the initial state. However, all of these states will be in a narrow-energy range because the channel interaction is strongly reduced for these states because they have mostly high- l character. It will be difficult to observe the final resonance states that have unmixed low- l character from initial strongly

l -mixed states. There are two reasons for this. The first is that the oscillator strength to the low- l states will be roughly a factor of $\sim \sqrt{-2\epsilon} = 1/n$ smaller than to the strongest state; the second is that the oscillator strength to a low- l state will typically be spread over a larger energy range due to their faster autoionization rate.

Thus, the expectation is that when starting from a low- l state the cross section may contain relatively broad features from low- l final states or a large number of sharp features from strongly l -mixed states or a combination of both; but when starting from a strongly l -mixed state, only a few sharp features will be readily observable. Of course, there will also be intermediate cases which do not conform to the examples discussed in the preceding paragraph. These may have the most interesting properties but the correlation and excitation behavior should then be discussed on a case-by-case basis.

The following papers [13,14] present experimental results that largely confirm this analysis. The Mg spectra [13] almost exactly follow the behavior sketched in this section. The Ba spectra [14] are more problematic due to complications from short-range $5dnl$ states perturbing the $6snl$ Rydberg states and from shape resonances in the $6pnf$ final states; thus, it is possible that a substantial fraction of the dipole matrix element arises from the fraction of the initial state that has perturber character. Reference [14] gives a fuller discussion.

IV. SUMMARY

In this paper a basic theory of isolated core excitations has been given for the case when the Rydberg atom is in a static field. The formalism gives the dipole matrix elements in terms of the properties of the wave function near the core. The method is expected to be very accurate and easily applicable to calculations of isolated core excitations in static electric or magnetic fields or a combination of the two. In the following two papers [13,14], we present detailed comparisons of *ab initio* calculations to experimentally measured isolated core spectra for Mg and Ba in a static electric field.

An approximation to the method for an atom in a static electric field allowed an analysis of the expected properties of the isolated core spectrum. The approximate form of the matrix element was composed of a sum over terms containing the difference of the WKB phase at the initial and final energy. This intriguing result may also hold, but in a generalized form, for isolated core excitations in fields for which the Hamiltonian is not separable. Further studies of isolated core excitation in different types of fields may provide an interesting window into how the core mediated channel interactions affect atomic Rydberg states.

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APPENDIX: ICE IN ZERO FIELD

The theory for ICE in zero field has been described many times so it will only be presented briefly with enough details for the similarities with the theory for ICE in a static electric field to be apparent. The formulas for ICE are simplest to derive when the initial state is a simple Rydberg state outside of the core and the final state is a two channel system with one closed and one open channel. I will denote the initial core state as Φ_i and the final core state as Φ_f .

The initial wave function may be written as $\Psi_i = \Phi_i F_i(r)/r$ when the Rydberg electron is outside of the core region; the function F_i may be written in terms of the regular and irregular Coulomb functions [8] as

$$F_i(r) = [\cos(\pi\nu_i)f_i(r) + \sin(\pi\nu_i)g_i(r)]/\nu_i^{3/2}, \quad (\text{A1})$$

where ν_i is the effective quantum number and is defined by $\nu_i = 1/\sqrt{-2\epsilon_i}$ when ϵ_i is the energy of the Rydberg electron. This form is necessary in order that the wave function goes to zero as r goes to infinity.

The final wave function may be written as the sum of two terms; a bound wave in the closed channel and a continuum wave in the open channel: $\psi_f = [\Phi_i C_i(r) + \Phi_f B_f(r)]/r$. The continuum wave arises because the core and the Rydberg electron can interact; the Rydberg electron can gain energy from the core and escape the atom while causing the transition $\Phi_f \rightarrow \Phi_i$. The continuum function C_i and the bound function B_f may also be expressed in terms of Coulomb functions; most importantly

$$B_f(r) = [\cos(\pi\nu_f)f_f(r) + \sin(\pi\nu_f)g_f(r)]A_f(E), \quad (\text{A2})$$

where A_f is an energy-dependent coefficient that depends on the coupling between the open and closed channels in the final state and $\nu_f = 1/\sqrt{-2\epsilon_f}$ with ϵ_f being the energy of the Rydberg electron.

If we use the assumption that the photon causes a transition in the core, then the dipole matrix element between the initial and final state is

$$d(E) = D_{fi} \int_{r_0}^{\infty} B_f^*(r) F_i(r) dr \quad (\text{A3})$$

[compare to Eq. (3)] where $D_{fi} = \langle \Phi_f | D | \Phi_i \rangle$ is the dipole matrix element for the core transition. As in [16], the product

$$B_f^* F_i = -\frac{1}{2} \frac{d}{dr} W(F_i, B_f^*) / (\epsilon_f - \epsilon_i), \quad (\text{A4})$$

where the Wronskian $W(A, B) = AB' - A'B$. The difference in energy in the Rydberg channels is the difference in the photon energy from the transition energy of the core state: $\epsilon_f - \epsilon_i = \omega - \omega_{fi}$ where ω is the photon frequency.

The result from Eq. (A4) should be substituted into the equation for the dipole matrix element to show that $d(E) = D_{fi} W(F_i, B_f^*) / [2(\epsilon_f - \epsilon_i)]$. The final expression may be obtained by using the forms for the radial functions and using the Wronskian properties of the Coulomb functions [20] giving

$$d(E) = \frac{A_f^*(E) D_{fi} \sin[\pi(\nu_f - \nu_i)]}{\nu_i^{3/2} \pi (\epsilon_f - \epsilon_i)}. \quad (\text{A5})$$

[compare to Eq. (10)]. This equation is interesting because it separates the contribution to the dipole matrix element into a factor from the final-state interactions $A_f(E)$, a factor from the core transition D_{fi} , and a factor that only depends on the energy difference of the Rydberg electron in the initial and final state. Note that the only factor that is really atom dependent in this two-channel model is the $A_f(E)$ since D_{fi} is energy independent.

It is instructive to rederive this result from a multichannel quantum-defect formalism. In this formalism, the wave functions do not have the physical asymptotic behavior as $r \rightarrow \infty$; typically, all wave functions diverge in the closed channels. It is only at a later stage in the calculation that the proper asymptotic behavior is imposed. The initial-state wave function is now written as

$$\bar{\psi}_i = \Phi_i [f_i(r) - g_i(r) \tan(\pi\mu_i)]/r \quad (\text{A6})$$

[compare to Eq. (5)] where μ_i is the quantum defect and the two linearly independent final state functions are written as

$$\bar{\psi}_j = \sum_{j'} \Phi_{j'} [f_{j'}(r) \delta_{j',j} - g_{j'}(r) K_{j',j}] / r \quad (\text{A7})$$

[compare to Eq. (6)] where $K_{j',j}$ is the K matrix that contains the information about the coupling between the closed and open channels.

Using the same assumptions about the dipole excitation, we obtain

$$d_j(E) = \frac{1}{\pi} \sum_{j'} [\delta_{j',j} \tan(\pi\mu_i) - K_{j',j}] D_{j'i} / (\epsilon_{j'} - \epsilon_i) \quad (\text{A8})$$

[compare to Eq. (8)] for the dipole matrix element. To obtain the original expression for the dipole matrix elements, it is necessary to normalize the initial wave function by multiplying it by $N_i = \cos(\pi\mu_i) (-1)^n / \nu_i^{3/2}$. It is also necessary to note that both of the final-state functions diverge in the closed channel and it is necessary to superpose the two solutions to eliminate the divergence; the proper superposition, $\psi_f = \gamma_i \bar{\psi}_i + \gamma_f \bar{\psi}_f$, is achieved when the coefficients have the properties: $K_{fi} \gamma_i + K_{ff} \gamma_f = -\sin(\pi\nu_f) A_f(E)$ and $\gamma_f = \cos(\pi\nu_j) A_f(E)$. Using these expressions, one can show the equivalence $d(E) = N_i [\gamma_i^* d_i(E) + \gamma_f^* d_f(E)]$.

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small for quasibound states at energies well below the classical ionization threshold. Treating the $A_{i\alpha}$ as if they were zero as $|\mathbf{r}| \rightarrow \infty$ introduces a negligibly small error in this case.

- [16] Because the Rydberg wave functions are all solutions of the same Hamiltonian, the following relations hold:

$$\begin{aligned} B_{i\beta}^* A_{i'\alpha} &= [(H_F B_{i\beta})^* A_{i'\alpha} - B_{i\beta}^* (H_F A_{i'\alpha})] / (\epsilon_{i\beta} - \epsilon_{i'\alpha}) \\ &= -\frac{1}{2} [(\nabla^2 B_{i\beta})^* A_{i'\alpha} - B_{i\beta}^* (\nabla^2 A_{i'\alpha})] / (\epsilon_{i\beta} - \epsilon_{i'\alpha}) \\ &= -\frac{1}{2} \nabla \cdot [(\nabla B_{i\beta})^* A_{i'\alpha} - B_{i\beta}^* (\nabla A_{i'\alpha})] / (\epsilon_{i\beta} - \epsilon_{i'\alpha}). \end{aligned}$$

- [17] There have been several applications of R -matrix ideas to non-hydrogenic atoms in magnetic fields. For an example, see M. H. Halley *et al.*, J. Phys. B **25**, 1775 (1993); For an application to crossed electric and magnetic fields, see J. Rao and K. T. Taylor, *ibid.* **30**, 3627 (1997).
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