Field ionization of Rydberg atoms for high-brightness electron and ion beams

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We present an ionization mechanism for use in a cold atom electron source with the goal of producing highly monochromatic electron beams. We experimentally produce a map of the Stark states of ^85Rb below the ionization threshold and identify states that undergo selective field ionization. The properties of an electron beam produced by field-assisted ionization of such states are quantified. A theoretical framework is established to predict the improvement to beam quality when ionization is conducted above the ionization threshold, where ionization conditions are typically more favorable than below the threshold. Calculations suggest that selective ionization of Rydberg states may offer a pathway to the production of high-brightness, highly monochromatic ion and electron beams.

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I. INTRODUCTION

Monochromatic electron beams are critically important for structuring and analysis of materials, from nanofabrication via electron-beam milling to compositional and structural analysis using electron energy loss spectroscopy (EELS). The advent of aberration-corrected optical systems has reduced limitations previously placed on electron-beam probe sizes by polychromatic beams at high energies (>100 keV), but at low energies, chromatic aberration is usually the limiting parameter [1]. High-resolution electron energy loss spectroscopy (HREELS), which combines EELS with highly monochromatic beams, can produce elemental maps with atomic resolution and probe the nature of atomic bonds in a variety of materials. The current standard for a highly monochromatic beam is an energy spread of less than 0.2 eV, which allows for observation of surface plasmons of gold nanoparticles [2] and the spectroscopic detection of single atoms [3]. More recently, monochromatic electrons have allowed atomic resolution to be realized in a transmission electron microscope operating with a beam energy of 15 keV [4].

Electron energy resolution of less than 0.1 eV is required to control and orient chemicals in the condensed phase [5,6]. State-of-the-art cold field emitting sources produce 100 keV electrons with an energy spread ΔU = 0.3 eV [7] and hence still require energy filtering. Monochromators are well developed but nevertheless complicated and, critically, rely upon removing a significant fraction of the electrons from the beam, thus limiting the beam current.

Recently, a new source of electrons based on the ionization of laser-cooled atoms has emerged. Careful ionization of an atomic ensemble, either directly or via a field-assisted process, produces inherently cold electron bunches, giving an impressively small transverse energy spread [8,9]. Electron beams with energies of U = 1–10 keV [10,11] have been produced by ionizing atoms in a static electric field, with the finite size of the ionization volume giving rise to a longitudinal energy spread on the order of 0.01% of the beam energy (ΔU = 0.1–1 eV). One possible mechanism to achieve reduced energy spread is field ionization of highly excited Rydberg atoms [12]. Under certain conditions, Rydberg atoms will ionize only at a specific value of the electric field. By using high field gradients, the length scale over which a beam of atoms will ionize can be very small, greatly reducing the energy spread of the beam.

Here we investigate the suitability of field-assisted ionization of rubidium Rydberg atoms for creating highly monochromatic electron and ion beams. We produce a high-resolution map of the Stark states below the ionization threshold and observe states which selectively ionize. For a particular selectively ionizing state, we predict the expected reduction in energy spread for an electron beam produced via selective field ionization. Finally, we model the effects of selective-state ionization for above-threshold Stark states, which are known to have higher ionization rates, to investigate the possibilities for further reducing the energy spread.

II. BACKGROUND

In HREELS, the energy resolution of the electron beam is not only critical to determining the structure that can be resolved, but also for improving the spatial resolution of bright field images [13], which is often limited by chromatic aberration. For a focused electron beam, the combination of beam emittance and aberrations arising from the source and the optical system determine the minimum achievable spot size. The dominant aberrations in the context of focused beams are spherical and chromatic. Spherical aberrations are a consequence of the optical system used, whereas chromatic aberrations and beam emittance are properties of the source. A common measure for the minimum achievable spot size is the beam diameter d_{50}, which is the diameter within which 50% of the beam current is encapsulated. With Gaussian distributions of both the beam energy U and the convergence angle α,

\[ d_{50} = \sqrt{(d_{50,x}^2 + d_{50,y}^2)^{1/2} + d_{50,c}^2}, \]  \hspace{1cm} (1)
where \( d_{50,c}, d_{50,e}, \) and \( d_{50,c} \) are the beam diameters arising from the spherical aberration, emittance, and chromatic aberration, respectively [14]. Spherical aberration arises due to a differing focal length as a function of position from the optic axis. Emittance is a measure of the transverse phase-space volume occupied by the beam, which characterizes both the lateral size and angular divergence of the beam, and thus its inherent focussability. Chromatic aberration is the variation in focal length for particles of different energy. The chromatic aberration spot size \( d_{50,c} \) is proportional to the energy spread of the beam \( \Delta U \) and is given by [15]

\[
d_{50,c} = \zeta c \Delta \alpha \frac{\Delta U}{U_0},
\]

where \( \zeta \) is a numerical constant for a given system [16], \( c \) is the aberration coefficient of the lensing system, and \( U_0 \) is the mean beam energy. It is clear that increasing the beam energy will reduce \( d_{50,c} \), but for many applications higher beam energies are not desirable. Consequently, the only method to minimize \( d_{50,c} \) is to reduce \( \Delta U \).

The Cold Atom Electron Source (CAES) produces inherently cold electron bunches. The transverse beam properties have been investigated in detail, and the beam emittance measured to be a few nmrad for millimeter-sized beams [17,18], orders of magnitude lower than other sources. Consequently, the CAES will have a much smaller value of \( d_{50,c} \) and given comparable values of \( d_{50,c} \) and \( d_{50,e} \), the CAES promises values of \( d_{50} \) below the current state-of-the art [19]. In contrast to the transverse beam properties, the longitudinal beam properties have hitherto remained largely unstudied, despite the relative simplicity with which the CAES can produce highly monochromatic electron beams.

In a CAES, ionization typically occurs in a region with width \( \Delta_z \) determined by the spot size of the ionizing laser beam and can be as small as 10 \( \mu \)m. Given an extraction field of strength \( F \) which is created by electrodes separated by distance \( d \) the energy spread can be expressed as

\[
\frac{\Delta U}{U_0} = \frac{\Delta_z}{d}.
\]

Reduction of this value could in principle be achieved by reducing the photoionization laser beam size through the use of high-numerical-aperture optical systems, but these are not always feasible and the ionization width \( \Delta_z \) will still be constrained by the diffraction-limited spot size. Using Rydberg atoms and the combination of a high-gradient electric field with a rapidly ionizing state may allow ionization widths of hundreds of nanometers or below, reducing the fractional energy spread by one to two orders of magnitude. If achieved, a system would effectively be “super-resolution,” with electron emission spot sizes below the optical diffraction-limited spot sizes of the photoexcitation lasers.

Use of Rydberg atoms for the creation of monochromatic beams was first proposed in Ref. [20], but its application in the context of CAESs was first proposed in Ref. [12]. The scheme proposed there involves the creation of a beam of Rydberg atoms that enters into a high-gradient electric field. The atoms are ionized once the field value is large enough to permit field-assisted ionization. In principle, the \( \Delta_z \) would then be limited by the gradient of the electric field. In practice, the evolution of Rydberg states through the electric field results in state mixing, leading to a range of threshold electric-field values and ionization rates. The degree to which Rydberg states mix is highly variable. Selective field ionization occurs when a state displays minimal mixing, and also rapidly ionizes near a specific value of the electric field [21]. By addressing states that undergo selective field ionization, it may be possible to reduce \( \Delta_z \) well below optical diffraction-limited spot sizes.

A key parameter in the study of the ionization of Rydberg atoms is the saddle-point energy \( E_{sp} \). A neutral beam of rubidium propagates along \( y \), before entering a region of electric field produced between plates separated by 50 mm. Coupling to the Stark states is achieved with excitation and Rydberg laser beams, which are directed perpendicular to the field with polarizations parallel to the field. Ions are detected 680 mm downstream. Inset shows a plot of the electron potential versus position, showing the saddle-point energy \( E_{sp} \).

**FIG. 1.** A schematic of the experiment to produce Stark maps of \(^{85}\text{Rb}\). (a) A neutral beam of rubidium propagates along \( y \), before entering a region of electric field produced between plates separated by 50 mm. Coupling to the Stark states is achieved with excitation and Rydberg laser beams, which are directed perpendicular to the field with polarizations parallel to the field. Ions are detected 680 mm downstream. Inset shows a plot of the electron potential versus position, showing the saddle-point energy \( E_{sp} \). (b) The energy-level diagram for \(^{85}\text{Rb}\).
in Fig. 1. A neutral beam of rubidium effuses from an oven before passing through an aperture of φ2 mm (where φ denotes diameter) and subsequently a 70 mm differential pumping tube of φ7.5 mm, and free-space propagates for 940 mm before entering the ionization region. An electric field is produced between two electrodes separated by 50 mm with φ940 mm before entering the ionization region. An electric field, the laser wavelength was reset and allowed 10 ms for 750 ms at each point. For each change in the value of the electric field, we expect minimal coupling to Stark states, with the calculations of Stark states, with mj = 1/2 states shown in blue (dark gray) and mj = 3/2 states in yellow (light gray). Because the value of the electric field at the position of the atoms is not known precisely, a single value offset was applied to the measured field values to obtain agreement between the data to the calculations. It should be noted that the electric-field values used to produce the density plot in Fig. 2 are the mean of the measured field values recorded over the duration of each given scan. The variation in the measured field values relative to the mean-field value was approximately 0.1%. There is good agreement between predictions and observations, with mismatch attributable to field jitter, field inhomogeneity, and drift in the wavelength calibration.

The theoretical locations of Stark states were computed following the method detailed in Ref. [31]. The method numerically calculates the energy eigenvalues for a Hamiltonian of the form

\[ \hat{H} = \hat{H}_0 + F \hat{z}, \]

where \( \hat{H}_0 \) is the Hamiltonian for the valence electron in the presence of the ionic core and \( F \hat{z} \) is a perturbation due to the electric field of strength \( F \) directed along \( z \). For excitation from the \( 5P_{3/2} \) states, we expect coupling to the \( nS_{1/2}, nD_{3/2} \), and \( nD_{5/2} \) states. With the probe laser polarization parallel to the electric field, we expect minimal coupling to \( mj = 5/2 \) states, which are not observed in Fig. 2. The states were computed for 400 field values between \( F = 550 \text{ V/cm} \) and \( F = 650 \text{ V/cm} \) with 2000 states included in the calculation.

IV. SELECTIVE FIELD IONIZATION

Critical to the production of a monochromatic beam is the identification of states that experience a rapid growth in the ionization rate or, equivalently, a dramatic broadening of the resonance peak. One such process that can result in localized growth in the ionization rate is interference narrowing, which occurs when two Stark states that are coupled to the continuum with the same autoionization rates experience an anticrossing [32]. The coupling to the continuum for one of the eigenstates will vanish and the coupling for the other eigenstate will be enhanced due to the interference between the coupling amplitudes that govern their ionization. Such observations have been made previously in sodium [24,29], rubidium [33,34], and in cesium [35,36].

Another process that can result in localized growth in the ionization rate is when a stable “blue” state (\( \Gamma \approx 0 \)) couples to a degenerate “red” state(s) (\( \Gamma \gg 0 \)) which is (are) unbound, resulting in rapid ionization around the crossing [24]. An example of this latter behavior can be seen in Fig. 3, which shows a section of the Stark diagram in the region around

Figure 2 shows the map of Stark states for 85Rb, both measured and calculated. The density plot displays the log (base 10) of the detected rate of ionization events, which has been normalized so the most rapidly ionizing state (measured at a rate of 17 kHz) appears black, with white indicating that no counts were detected. Background counts are expected from photoionization of Rydberg states and blackbody ionization while Penning ionization is not expected to contribute due to the low density. The measured rates of ionization are overlaid with the calculations of Stark states, with mj = 1/2 states shown in blue (dark gray) and mj = 3/2 states in yellow (light gray). Because the value of the electric field at the position of the atoms is not known precisely, a single value offset was applied to the measured field values to obtain agreement between the data to the calculations. It should be noted that the electric-field values used to produce the density plot in Fig. 2 are the mean of the measured field values recorded over the duration of each given scan. The variation in the measured field values relative to the mean-field value was approximately 0.1%. There is good agreement between predictions and observations, with mismatch attributable to field jitter, field inhomogeneity, and drift in the wavelength calibration.

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The combination of an optimized neutral atomic beam and adjacent regions of highly uniform electric fields with regions of high field gradient should allow creation of a high-quality beam of Rydberg atoms that can be efficiently ionized with a small ionization region (small $\Delta_r$).

We assume an atom within the atomic beam traveling at speed $v$ is excited to a Rydberg state $|\Psi\rangle$ in a uniform field of strength $F_0$ and propagates through a region with a high field gradient. Assuming the field is aligned along the $z$ axis with a gradient of $\zeta$, the field is then given by $F(z) = F_0 + \zeta z$.

We define the effective ionization width $\Delta_{\text{eff}} = 1/2(z_+ - z_-)$ as the region over which 68.2\% of the atoms are ionized:

$$\Delta_{\text{eff}} = \frac{1}{2}\int_{z_-'\text{ to } z_+'} |\mathcal{P}(F)|^2 dz,$$

(5)

allowing for direct comparison with $\Delta_r$, typically defined as the standard deviation of the ionization laser spatial profile. $\mathcal{P}(F)$ denotes the cumulative probability that the atom will be ionized at a field between $F_0$ and $F$ after having been excited in a field of strength $F_0$:

$$\mathcal{P}(F) = 1 - \exp\left[\frac{1}{\zeta v_z} \int_{F_0}^F \Gamma(F')dF'\right],$$

(6)

where $\vec{v}_z$ is the mean atomic velocity within the beam and $\Gamma(F')$ is the ionization rate of the Rydberg state $|\Psi\rangle$. In expressing the cumulative probability as a function of the field strength $F$, we assume the field is linear in $z$ and also that $t = (z - z_0)/\zeta v_z$. Provided the form of $\Gamma(F')$ is known, Eqs. (3) and (5) allow the energy spread of the beam to be calculated. We insist that, for an ionization scheme to be useful, that the cumulative ionization probability be near unity after the anticrossing. If this were not the case, any Rydberg atoms not ionized would continue to propagate into a high-field region where they would be ionized via an alternate mechanism, resulting in a complicated longitudinal energy distribution and a reduction in beam monochromaticity.

By using the above formulation, we can calculate $\Delta_{\text{eff}}$ for the state shown in Fig. 3, which shows the measured ionization rate as a function of the electric-field strength that was interpolated to produce an approximation of $\Gamma(F')$. The ionization rate is determined by the width $\sigma$ of the observed ionization peaks. In our apparatus, the maximum field gradient we can produce is on the order of $1 \times 10^9$ V/m$^2$. This value was calculated by using detailed modeling of the electrode system in SIMION [37] and shows the length scale over which the field has an appreciable gradient is 5 mm. Given a neutral rubidium beam produced from an oven at 373 K and an excitation field of 580 V/cm, with excitation to $|\Psi\rangle$ (Fig. 3), we calculate the ionization probability as a function of $F$ by using equation (6). A rapid growth in the ionization probability occurs over approximately 250 nm and as expected and continues to increase with increasing $F$. While a localized growth in ionization probability is observed over some hundreds of nanometers, the total number of ionization events in this region is extremely small, owing to the small ionization rates. Consequently, the majority of the ionization takes places at higher values of the electric field and hence results in a ionization over a range of positions (large $\Delta_{\text{eff}}$).

In contrast, the scale over which state $|\Psi_{ii}\rangle$ destabilizes is much shorter due to the highly localized growth of the
FIELD IONIZATION OF RYDBERG ATOMS FOR HIGH- . . . PHYSICAL REVIEW A 95, 063845 (2017)

FIG. 4. Ionization properties of a selectively ionizing Rydberg state in rubidium. (a) Predicted cumulative ionization probability of $|\psi_{ii}\rangle$ as a function of electric-field strength around $F = 585 \text{ V/cm}$. The blue shaded region from $\sigma_- = 15.9\%$ to $\sigma_+ = 84.1\%$ defines the region over which the beam ionizes. The color scale indicates the growth of ionization rate at the crossing, with $\eta = 1$ corresponding to $37 \text{ MHz}$. (b) Predicted ionization width as a function of the maximum ionization rate of $|\psi_{ii}\rangle$ at the crossing. The parameters for excitation and ionization are given in the text.

ionization rate. The exact growth in the ionization rate cannot be well predicted because no additional data were recorded in the region around the destabilization. Because there is no peak in the Stark map, we therefore include an enhancement of the ionization rate by a factor of $\eta$ at the anticrossing. Previously, the ionization rate in the region of the crossing was measured by Ref. [24] to increase under similar conditions by two orders of magnitude relative to the stable state ($\eta = 10^2$), with a greater growth predicted but not measured. Assuming the value of $\Gamma$ grows by a factor of $\eta$ to a maximum rate $\Gamma_M$ over the crossing, it is possible to calculate the expected value of $\Delta_{\text{eff}}$ given excitation to $|\psi_{ii}\rangle$, with all other parameters the same as were used to calculate the ionization width of $|\psi_{ii}\rangle$.

Figure 4(a) shows the cumulative ionization probability for a rubidium atom excited to $|\psi_{ii}\rangle$ in the region around $F = 584 \text{ V/cm}$. The different curves display how the cumulative ionization probability varies with the maximum ionization rate of $|\psi_{ii}\rangle$ at the anticrossing. It is clear that the ionization probability experiences highly localized growth and, as expected, with increased ionization rate the range of field values over which the ionization occurs decreases. In addition, a greater ionization rate also ensures near-unity ionization probability. For values of $\Gamma_M > 2.5 \times 10^9 \text{ Hz}$, we calculate $\Delta_{\text{eff}}$ to be on the order of $50 \text{ nm}$, far below the tens of microns typically achieved by using photoionization and in the super-resolution regime ($\Delta_{\text{eff}}$ of order $100 \text{ nm}$). Figure 4(b) shows the ionization width $\Delta_{\text{eff}}$ as a function of the maximum ionization rate $\Gamma_M$. With greater values of $\Gamma_M$, the ionization width decreases, but it is clear that large growth in the ionization rate, at least $\eta > 30$, is required to produce super-resolution values of $\Delta_{\text{eff}}$. For values of $\eta < 30$, values of $\Delta_{\text{eff}}$ near or below the diffraction limit are achievable; however, we are primarily interested in the super-resolution regime. A growth factor of $\eta = 30$, which corresponds to $\Gamma_M \approx 1 \times 10^8 \text{ Hz}$ is not entirely unreasonable; in other work, a growth value of $\eta = 10^2$ has been measured [24], and separately a value of $\Gamma_M = 1 \times 10^8 \text{ Hz}$ has been measured over a anticrossing [34]. A growth factor of $\eta = 30$ would yield a $\Delta_{\text{eff}} = 130 \text{ nm}$ and a higher growth rate, $\eta > 70$ (corresponding to $\Gamma_M > 2.5 \times 10^9 \text{ Hz}$), is required to achieve $\Delta_{\text{eff}} < 50 \text{ nm}$. However, for growth rates less than $\eta \approx 80$, the cumulative ionization probability is below unity, meaning that any atoms not ionized will undergo ionization in the high-field region downstream, subsequently reducing the monochromaticity and increasing $\Delta_{\text{eff}}$. This means that, for a monochromatic beam, we require a growth rate of at least $\eta = 80$, which would require an exceptional state with an ionization rate greater than that previously observed in Ref. [34]. Thus, in all likelihood, a sufficient value of $\Gamma_M$ would not be reached to simultaneously ensure both efficient ionization and a small ionization width.

Further measurements of $\Gamma_M$ are required to determine the suitability of state $|\psi_{ii}\rangle$ for monochromatic beam electron-beam production. The above results demonstrate that selective field ionization can result in ionization widths much smaller than conventional photoionization sources, but may come at the cost of ionization efficiency. One possible solution is to work in the region above the ionization threshold, where the transverse beam properties will be slightly degraded, but the ionization rates are typically many orders of magnitude higher. Provided an appropriate state with a localized growth in the ionization rate is used, a small ionization width could be combined with high-efficiency ionization. In the following section, we seek to validate this idea theoretically.

VI. MODELING ABOVE-THRESHOLD IONIZATION

The purpose of this section is to theoretically model the ionization rate for a state that experiences selective field ionization above the ionization threshold. We then seek to determine whether field ionization of Rydberg states is a viable method for highly monochromatic electron-beam production.

Calculation of the ionization width $\Delta_{\text{eff}}$ requires that we have precise knowledge of $\Gamma(F)$, and accurate prediction of the form of $\Gamma(F)$ is often difficult. In the case of hydrogen, the value of $\Gamma(F)$ can be calculated in a relatively straightforward manner [38], but for other atoms it is more complicated due to the coupling of states at the core and the associated avoided crossings of Stark states, though calculation of the lineshapes is possible [39]. For high-lying Rydberg states in alkali metals, the states of hydrogen provide a good approximation provided the quantum defect is small [40]. Since we are interested in the ionization rate of states near avoided crossings, we need only model the two-state system, provided the states are isolated.

More explicitly, to ensure the states are isolated, we require that the scale of the coupling between the states ($V_{ij}$) is less than the difference in energy to neighboring states. Given the principal quantum number $n$, the separation of states to first order can be approximated by $(3/2)n F$, within an $n$ manifold, before the first crossings with other $n$ manifolds. The first crossings occur at a field strength of $1/(3n^2)$, hence the minimum energy separation for different values of $n$ will vary as $1/(2n^4)$. The core coupling $V_{ij}$ can be approximated by using quantum-defect theory, where $V_{ij} \approx \delta_{ij}/n^2$ [21,41,42]. This suggests that, provided the quantum defect is small (less than 0.5), a two-level model should well approximate the system. In the case of rubidium, the $\delta_2$ defect value for the
Selective field-ionization processes above the ionization threshold usually occur when a stable “blue” state \(\Gamma \approx 0\) couples to degenerate “red” state(s) \(\Gamma \gg 0\) which are unbound, resulting in rapid ionization around the crossing; the field at which this occurs defines \(F_x\). We use a two-level model based on states of hydrogen \(A\) that allows for the calculation of \(\Gamma(F)\) around \(F_x\). A similar model has been previously used to obtain excellent quantitative agreement for the ionization rate of sodium near the anticrossing of the \(12, 6, 3, 2\) and \(14, 0, 1, 1, 2\) states \(24\) (labeled \([n, n_1, n_2, m]\)). By choosing states with a large value of \(|m|\), we can ensure a small value of \(\delta_2\) and hence expect our model to be valid. The primary criterion for state selection is that a stable blue state crosses an unstable red state, which for even moderate electric fields is very common. We choose the states \([17, 0, 13, 3]\) and \([14, 10, 0, 3]\), but it should be emphasized that these are not unique. There are a multitude of states that display similar properties; we choose these simply because they are experimentally compatible with our system. In reality, the exact states to be used would, in great part, be determined by the core coupling \(V_c\) between the two states. The value of \(V_c\) is critical to determining the lineshape of state-selective ionization and hence the ionization width \(\Delta\), but is not readily tunable, meaning that the crossing to be used must be selected for the appropriate value of \(V_c\).

Using Eq. \(6\), it is again possible to calculate the cumulative ionization probability for a Rydberg atom propagating into an electric-field gradient as described above. We calculate the probability of ionization as a function of the electric field near the crossing of the \([17, 0, 13, 3]\) and \([14, 10, 0, 3]\) states (Fig. 5), by using \(\Gamma \ldots(F)\) [Eq. \(A2\)] \(42\) and an excitation field of 6 kV/cm, with the other parameters as in Sec. V. With a coupling strength of \(V_c = \Gamma \ldots(F_x)\) the rapid growth of the ionization rate near \(F = F_x\) results in the rapid increase of the ionization probability, as was previously observed with below-threshold states. Due to the greatly increased ionization rate, on the order of \(10^{10}\) Hz, a much higher ionization efficiency is predicted. From these data, we extract the ionization width of \(\Delta_{\text{eff}} = 0.26 \mu m\) with unity probability for ionization. The value of \(\Delta_{\text{eff}}\) is consistent with a previous estimate of the reduction of the ionization width via selective field ionization, which showed an improvement of one to two orders of magnitude compared with nonselective field ionization, with \(\Delta_{\text{eff}} \approx 1 \mu m\) \(12\).

**V. CONCLUSION**

Mapping of the Stark states below the ionization threshold allowed for the observation of selective field-ionization states, but insufficient resolution in the data around the localized growth of the ionization rate limited our ability to determine the states’ suitability for the creation of a monochromatic electron beam. Further work is required to determine whether localized growth of the ionization rate below the ionization threshold is sufficient to allow for simultaneously efficient and localized ionization. It is possible that the low-ionization rates typical of states below the threshold will limit their usefulness in creation of monochromatic electron beams. Above the threshold, where ionization rates are much larger, we predict values of \(\Delta_{\text{eff}} \lesssim 260 \text{ nm}\) are readily achievable. An ionization width on the order of hundreds of nanometers represents an improvement by a factor of at least ten compared with direct photoionization. Using high-numerical-aperture in-vacuum lenses permits laser spot sizes of the order a few microns, but getting below this limit represents a major challenge. By using field-assisted ionization of Rydberg atoms, any reduction in the ionization width linearly improves the beam monochromaticity, commensurate with a reduction of the value of \(d_{50}\). If such a super-resolution ionization scheme were realized, it would result in an electron beam with a relative energy spread better than 1 part in \(10^5\), removing the need for a monochromator for many experiments. By implementing a high-efficiency photoexcitation scheme, for example, one similar to that already implemented in a cold atom source \(44\), this would allow for the creation of a high-current highly monochromatic electron beam. Additionally, the application of the same system to focused ion-beam liquid-metal ion sources would be extremely powerful. For example, in a 30 kV cold atom beam ion source operating in low-current mode (0.1 pA), the expected value of \(d_{50}\) is 200 pm \(19\) when using photoionization. This value could potentially be reduced to \(d_{50} = 50\) pm by using Rydberg ionization. Likewise, a field-ionization source operating in high-current mode (1 nA) could reach \(d_{50} = 4\) nm, a factor ten below current state-of-the-art liquid-metal ion sources.

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APPENDIX: MODELLING AVOIDED CROSSINGS

We seek to estimate the form of the ionization rate for a given state as a function of the electric field. We consider the crossing of a stable blue state with an unstable red state. The Hamiltonian is then given by

\[
\hat{H} = \begin{pmatrix} -\delta/2 & V_c \\ \delta/2 - i\Gamma/2 & \end{pmatrix},
\]

where \( \delta \) and \( \Gamma \) are the usual parabolic quantum numbers. By calculating \( \delta \), one can calculate a value of \( \delta \) and, in conjunction with Eq. (A3), the ionization rates of the mixed system \( \Gamma_{\pm} \) can be calculated near the anticrossing.

By using quantum-defect theory one can estimate the expected core coupling [41] but, as a general trend, if the coupling is too weak, no strong state mixing is observed and narrowing either does not occur or only weakly occurs, resulting in no growth in the ionization rate. For stronger couplings, the effect begins to become delocalized and a growth in the ionization rate is seen over a range of field values. In the context of achieving highly localized ionization, the latter is highly undesirable. The maximum coupling rate occurs for any value of \( V_c > \Gamma/4 \), with the minimum ionization width and the maximum ionization rate simultaneously occurring for \( V_c = \Gamma/4 \). Physically, the actual value of coupling cannot be tuned as a simple parameter, but rather will be determined by the states in question. Some degree of tunability is present by changing the value of \( n_1 \) for the red state, moving to a neighboring crossing. If no states with desirable properties and appropriate coupling can be found, then the crossing of a different blue state should be considered. In practice a model, such as the one presented here, would be used to find potentially appropriate states and then a high-resolution scan performed experimentally to identify the optimum states.

\[ \Gamma = \frac{4R^{2\delta_1+m+1}}{n_1^2n_2!(n_2+m)!} \exp \left\{ -\frac{2R}{3} - \frac{n_1^2}{4} \left[ 34(n_2^2 + n_2m) + 46n_2 + 7m^2 + 23m + \frac{53}{3} \right] \right\}. \]