Resonant charge transfer of hydrogen Rydberg atoms incident at a metallic sphere

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Abstract

A wavepacket propagation study is reported for the charge transfer of low principal quantum number \((n = 2)\) hydrogen Rydberg atoms incident at an isolated metallic sphere. Such a sphere acts as a model for a nanoparticle. The three-dimensional confinement of the sphere yields discrete surface-localized ‘well-image’ states, the energies of which vary with sphere radius. When the Rydberg atom energy is degenerate with one of the quantized nanoparticle states, charge transfer is enhanced, whereas for off-resonant cases little to no charge transfer is observed. Greater variation in charge-transfer probability is seen between the resonant and off-resonant examples in this system than for any other Rydberg-surface system theoretically investigated thus far. The results presented here indicate that it may be possible to use Rydberg-surface ionization as a probe of the surface electronic structure of a nanoparticle, and nanostructures in general.

Keywords: Rydberg, charge transfer, nanoparticle

(Some figures may appear in colour only in the online journal)

1. Introduction

Resonant charge transfer from a Rydberg atom to a metallic structure has been extensively studied theoretically and experimentally. Previous studies have primarily focused on understanding how the properties of the Rydberg atom, such as the principal quantum number \(n\), the parabolic quantum numbers \(k\) and the collisional velocity, affect the resulting charge-transfer dynamics \([1–4]\). When a conducting metal surface is used, the conduction band of the metal is normally degenerate with the experimentally accessible Rydberg energies, and therefore the charge transfer from the Rydberg atom to the surface is resonantly enhanced. In this situation the surface-ionization process is largely independent of the surface electronic structure, such that two conducting metal surfaces, such as gold and aluminium, would be expected to show very similar behaviour.

However, surface-ionization studies using doped silicon surfaces \([5]\), insulating thin films \([6]\), dielectric materials \([7]\) and adlayers indicate that resonant charge transfer is sensitive to the electronic and geometric structure of the surface. The recent experimental studies from our group, in which Rydberg atoms have been used as a probe of high-lying discrete image states at projected band gap surfaces \([8, 9]\) and thin metallic films \([10]\), are of particular relevance to the system described in this paper.

An electron in a thin metallic film is confined along the surface normal direction like a particle in a one-dimensional box, and has a discrete series of states protruding into the vacuum from the surface. A recent study from our group showed resonance-enhanced charge transfer when hydrogen Rydberg atoms incident at an iron thin film were degenerate with these thin-film states \([10]\). Varying the thickness of the thin film changed the incidence of resonances as a function of Rydberg principal quantum number, and the intensity of the surface ionization signal indicated that the thin-film wavefunctions had substantial image-state character (see section 2.1 for further discussion of image states). As nanostructures in general are confined on a nanoscale along one or more dimensions, it is expected that discrete surface-localized states are a general feature of nanostructures, and that the resonance-enhanced charge transfer seen for thin films could be extended to other systems with discrete states at the energies of the Rydberg atoms.
For the thin metallic films, the motion of the electron is effectively unconfined in the direction parallel to the thin film surface, and therefore there is a continuum of energy levels stacked on each one-dimensional energy level associated with the perpendicular dimension. The parallel momentum of the electron is zero at the base of each stack and increases as the overall energy increases. Therefore the charge transfer is never truly non-resonant but there is a marked preference for transfer to zero-parallel-momentum states and therefore resonance effects are still observed.

In this paper we move from the one-dimensional confinement of a thin film, to the three-dimensional confinement of a metallic sphere. In this case the energy distribution of the quantum states changes—the states are truly discrete—and there is no longer a continuum available for off-resonance states to couple to. As a result much stronger differences between the resonant and off-resonant cases would be expected. The isolated metallic sphere is a good model for single metal nanoparticles, and the results presented in this paper for incidence of Rydberg H atoms at such nanoparticles indicate that resonance-enhanced charge transfer occurs between degenerate hydrogen atom states and surface localized states of metallic nanoparticles.

2. Background and theoretical methods

2.1. Image states

The presence of an electron outside of a flat metallic surface induces an image charge. The interaction of this external electron and its image charge is described by an image-charge potential, which yields a discrete, Rydberg-like series of potential, which yields a discrete, Rydberg-like series of image states. The electronic image-state wavefunctions are localized at the surface-vacuum interface (ψ → 0, ze → ±∞, where ze is the electron position relative to the surface). The image state potential is attractive and Coulomb-like, \( V(ze) = -\frac{1}{2}(z_e - z_{im})^{-1} \), where \( z_{im} \) is the image plane position. The energies of the image states obey the Rydberg formula (with \( Z = 1/4 \)):

\[
E_{\text{IS}}^{\text{img}} = -\frac{1}{Z^2} \frac{1}{2(2n_{\text{img}} + a)^2},
\]

where \( n_{\text{img}} \) is the image-state index and \( a \) is the quantum defect parameter for a given surface. Image states protrude into the vacuum region from the surface and the 1D wavefunctions have the form [11]

\[
\psi_{\text{IS}}^{\text{img}}(z_e) = z_e R_{\text{IS}}^{\text{img}}(z_e/4),
\]

where \( R_{\text{IS}}^{\text{img}}(z_e/4) \) is the normalized hydrogenic (s-wave) radial wavefunction. The expectation value for the electron position shows how the wavefunction extends well into the vacuum \( \langle z_e^2 \rangle_{\text{IS}} = 6(n_{\text{img}} + a)^2 a_0^3 \), such that there can be significant overlap with the electronic wavefunction of an incident Rydberg atom at a long distance from the surface, leading to resonance-enhanced charge transfer.

The discrete image states are mixed and broadened when degenerate with a band, such as in a conducting metal (e.g., gold or aluminium) leading to the generic surface-ionization behaviour described earlier [1, 2]. In this case all the surface-localized states have a little image-state character and are known as image resonances. However the image states form a discrete long-lived series at projected-band-gap surfaces. \( n = 25–34 \) hydrogen Rydberg atoms incident at a projected-band-gap Cu(100) surface were shown to exhibit resonance-enhanced charge transfer for principal quantum numbers when the Rydberg atom was degenerate with an image state of the surface [9]. The intensity of surface-ionization signal measured for an off-resonant Rydberg state was similar to that expected for a hydrogen atom at a conducting metal surface. For the resonant hydrogen atoms at the Cu(100) surface a true enhancement in surface ionization was seen, owing to the better spatial overlap of the wavefunction of the incoming Rydberg atom with the image state wavefunction, than for the broad image resonances of a fully conducting system. These experimental findings were successfully predicted and modelled using a wavepacket-propagation approach similar to the one used in this paper [8]. As discussed below, in the case of a metallic sphere the image states still exist (although an angular function must be included in equation (2) to describe their 3D form) but are mixed with the internal quantum states of the 3D well leading to states with mixed image-state and 3D well-state character.

2.2. Previous studies of nanoparticle energy levels

Rinke et al theoretically investigated the image states of spherical metal clusters, or small nanoparticles [12]. Finite numbers of wavefunctions were determined due to the confinement of the potential and the wavefunctions contracted to those of the bulk metal with increasing nanoparticle radius. Their model is used in this work, and our derived nanoparticle energy levels and wavefunctions are consistent with their results.

Kasperovich et al have experimentally investigated electron capture by the image states of metal nanoparticles [13]. A beam of electrons was produced by an electron gun and crossed a beam of sodium nanoclusters. Electron capture by the image states charged the nanoparticle and gave it a magnetic moment, which allowed it to be steered off course by a large applied magnetic field. Neutral nanoparticles were fragmented and ionized by UV light and counted by an ion detector. Ultimately the electron capture cross-section between the nanoparticle and the electron was determined by the signal depletion when the electron gun was turned on. The electron capture cross-section gave an indication of the size of the nanoparticle to within 20%.

To our knowledge, the only experimental study investigating Rydberg surface ionization at nanoparticles was carried out in our laboratory [14]. A beam of hydrogen atoms was excited in the range \( n = 26–34 \) and was incident on a monolayer of nanoparticles of radius \( R \approx 5 \) nm laid down on a Si wafer. The clearest finding from this work was a \( k \)-state change for the extreme blue-shifted Rydberg atoms as they approached the surface i.e. the surface ionization profiles of the \( n, k = n - 1 \) states resembled the \( n + 1, k = -n + 1 \)
surface ionization profiles. This was attributed to the curvature of the electrostatic field lines near the nanoparticle and the resultant state-mixing as the Rydberg atom passes through this inhomogeneous field. No resonance enhancement of charge transfer was seen at specific principal quantum numbers, but surface analysis revealed some areas of exposed substrate and clustering of the nanoparticles on some of the surfaces, such that it was difficult to determine the relative contribution of charge transfer to an isolated nanoparticle or the silicon substrate within the measured signal.

The work in this paper represents the first theoretical study investigating the surface ionization dynamics of a hydrogen Rydberg atom at a nanoparticle. To our knowledge, no other previous theoretical or experimental studies have been carried out to investigate the charge transfer of negative ions or Rydberg atoms at a nanoparticle.

2.3. Wavepacket propagation

A wavepacket propagation approach has been used previously in our group to successfully model the charge transfer dynamics of hydrogen Rydberg atoms to a conducting metal surface [2] and a projected-band-gap surface [8]. Wavepacket propagation studies by other researchers have been used to model the related process of electron transfer to a surface from an anion at a thin metallic film [15] and a projected-band-gap surface [16].

The general implementation of the wavepacket propagation approach used in this work is described in [2, 8]. In outline, the initial electronic wavefunction of the Rydberg atom is determined via matrix diagonalization at atom-surface separations of \( D_0 \sim 6 \theta^2 \). A Lagrange–Laguerre discrete variable representation (DVR) is used for the radial coordinate \( \theta \geq 100 \) grid points, and a Legendre DVR for the angular coordinate, \( \theta \geq 100 \) grid points. For the propagation of the electronic wavefunction in time, the radial part of the initial electronic wavefunction is then projected onto a Coulomb wavefunction in time-evolution operator, which is approximated by a symmetric split operator [19], to the electronic wavefunction at the current time step results in the electronic wavefunction at the next time step. A time step of \( \Delta t = 1 \) a.u. is used throughout. The surface is moved towards the H atom at constant velocity. The value for the velocity chosen, \( v_1 = 3 \times 10^{-4} \) a.u. \( \equiv 656 \text{ m s}^{-1} \) unless otherwise stated, sits in the middle of the experimentally accessible range of velocities for experiments conducted in our laboratory [1, 9, 10]. The calculation time varies significantly from 30 min to 24 h on a single core of a quad-core pentium processor.

The grid is bound by a complex absorbing boundary to impose the correct outgoing boundary conditions and to remove any reflections of the wavefunction at the edge of the numerical grid [20]. The nanoparticle and the Rydberg atom are within the absorbing boundary for the duration of the propagation. The electron density on the Rydberg atom, which is defined as the electron density within the absorbing boundary and outside of the nanoparticle, is initially equal to 1, and is monitored as a function of atom-surface separation to study the extent of the charge transfer away from the Rydberg atom. The derivative of the electron density with respect to atom-surface separation corresponds to the surface ionization probability at the given distance.

2.4. The nanoparticle potential

The quantum states of small metallic clusters have been modelled by Rinke et al [12] and their potential is used here. Similar to a successful approach used in the flat surface case [2], the explicit form of the potential used to model nanoparticles in the region outside the nanoparticle is based on the classical image-charge model; it describes the interaction of the electron and the induced image charge at a metallic surface \( V_{\text{image}} \). The potential inside the sphere is equated to a jellium model of the bulk metal \( V_{\text{bulk}} \), and the potential is smoothly interpolated across the surface region using the function \( p(r) \). The electron-image electron potential is thus given by

\[
V_{\text{ee}} = \begin{cases} 
V_{\text{image}} & r > R + d \\
V_{\text{bulk}} & r < R - d,
\end{cases}
\]

where \( r \) is the distance between the electron and the nanoparticle centre, \( R \) is the radius of the nanoparticle and \( d \) is an interpolation region such that \( V_{\text{image}}(R + d) > V_{\text{bulk}}(R - d) \). The image potential and the bulk metallic sphere potential are approximated as

\[
V_{\text{image}}(r) \approx \frac{-R^3}{2r^3(r - R^2)},
\]

\[
V_{\text{bulk}} = \frac{V_0}{2A} \exp(B(r - R) + 1),
\]

where \( A \) and \( B \) are the jellium parameters for the bulk metal surface of choice [21].

The presence of the Rydberg ion core adds to the total potential experienced by the Rydberg electron in the presence of the nanoparticle

\[
V_{\text{total}} = V_{\text{ee}} + V_{\text{ep}} + V_{\text{pp}} + V_{\text{Coulomb}}.
\]

where \( V_{\text{ep}} \) is the combined repulsive image electron–ion and image ion–electron interaction, \( V_{\text{pp}} \) is the attractive image proton–proton interaction and \( V_{\text{Coulomb}} \) is the Coulomb interaction between the ion and the electron. As the Rydberg ion core is fixed in these calculations to lie along the normal direction to the nanoparticle surface, the explicit forms
of $V_p$ and $V_e$ are approximated to be the same as in the flat surface case [2].

For larger nanoparticles, such as the ones that have previously been investigated experimentally (e.g. $R = 10$ nm), the surface will behave more as a curved surface than a spherically confined system. In the limit of $R \to \infty$ then $V_{bulk} \to V_0$ where $V_0$ is the internal potential for the bulk free-electron metal in question. In effect, within this model, at large radii the nanoparticle forms a continuum of states, and behaves as a curved semi-infinite slab of jellium.

When modelling a confined potential of this type, the edge of the DVR grid must be located sufficiently far from the nanoparticle surface such that the grid boundary has no effect on the calculations. The resulting large grid leads to the nanoparticle calculations being computationally very expensive, and restricts the calculations to low principal quantum number Rydberg atoms and very small nanoparticles.

No attempt has been made in the work presented here to account for the substrate onto which the nanoparticles might be deposited in an experimental situation, or to the presence of surfactants and solvents on the surface due to the deposition process. Finally only the interaction between a single nanoparticle and a single Rydberg atom is considered, i.e. only the one-electron process is investigated; it is possible that significant further effects would be observed experimentally, associated with partial-monolayer coverage, interaction with multiple nanoparticles, clustering of nanoparticles or glancing interactions.

### 3. Results

#### 3.1. The energy levels and wavefunctions of a small metallic nanoparticle

Initially a series of diagonalizations were carried out to determine the distribution of the energy levels and the nature of the wavefunction of the vacant nanoparticle states, which are able to accept the donated Rydberg electron. The potential used to model the behaviour of an electron outside of a nanoparticle is described in section 2.4. A Hamiltonian is built by discretizing this potential onto a Sinc DVR grid, and the subsequent diagonalization of this Hamiltonian yields the well-image state energies and wavefunctions.

A nanoparticle, which is modelled as a fully isolated metallic sphere, behaves as a three-dimensional spherical quantum well [12]. An electron in a small nanoparticle behaves like a particle confined in a spherical box, yielding a discrete series of quantum states. These well-localized states are discrete, fully confined within the physical boundaries of the nanoparticle and the energetic spacing between neighbouring states increases with energy. For a small nanoparticle the well-localized wavefunctions are atom-like and there is no coupling possible between neighbouring states, which are widely spaced in energy.

As the dimensions of the nanoparticle increase, the energy gap between neighbouring states decreases as in the simplistic particle-in-a-spherical-box model, and ultimately the limit of a bulk material with a curved metallic surface is reached. The projected band structure of such a surface is different to its flat analogue, as a curved surface cannot result from cleavage of the bulk along a specified crystal plane.

The above picture describes the behaviour of the states of a spherical system confined by infinite potential walls. However, the nanoparticle states considered in this paper are not pure well-localized states—penetration of the wavefunction outside the physical boundary of the nanoparticle is possible. As described in section 2.1, an electron outside a metallic surface is bound by the image-charge interaction giving rise to Rydberg-like image-state series. For the metallic nanoparticle case, image-state character is mixed into the discrete series of spherical well-localized states, yielding a discrete series of states with hybrid well-image character. We refer to these as the ‘well-image states’. These states are long-lived due to the absence of an overlapping conduction band within the nanoparticle.

The radii of some of the nanoparticles investigated in this paper are just several atoms wide and in reality such species would form non-spherical metallic clusters. Our model treats these small molecules as perfect spheres of structureless jellium, which while being clearly unphysical, enables the investigation of physical trends which may be applicable to large more realistic sized particles and higher-$n$ Rydberg atoms.

Figure 1 plots the probability density for a selection of these well-image state wavefunctions for a $10a_0$ radius nanoparticle at a variety of energies. The probability density is calculated as $|\psi|^2$, where $\psi$ is the nanoparticle localized electronic wavefunction. The small-nanoparticle probability densities, shown in figure 1, are atom-like in character, and it is possible to attribute $n$, $l$ and $m_l$ quantum numbers to them. Pure well-localized states would be confined by the physical edge of the nanoparticle, depicted by the blue line in each figure. All of the wavefunctions in figure 1 have mixed well-image character, but individual wavefunctions have differing amounts of well-state character or image-state character, depending on the energy of the states. At very low energies, near the bulk-metal value of the nanoparticle well, states have more well-state character, but at higher energies when the spacing between image states becomes smaller, image-state character dominates. The first two wavefunctions in figure 1, with energies $E = -0.52$ and $-0.47$ a.u., are low $n$, $l$ states, with almost pure well-state character, as can be seen by the small amount of probability density extending beyond the blue line. In contrast, the higher $n$, $l$ states, with energies $-0.08$ and $-0.02$ a.u., have significant image-state character and extend significantly into the vacuum. The wavefunction of an electron occupying a high-lying hybrid well-image state would both occupy the nanoparticle itself, and protrude into the surrounding vacuum.

As the radius of the nanoparticle increases, there are more well states, but the same number of image states, such that there are more zero-order pure well states at low energies, and the hybrid well-image states typically have more well-state character. The electron wavefunction contracts to the nanoparticle surface as the radius of the nanoparticle increases [12], ultimately forming a conduction band within the nanoparticle, and the well-image states become image resonances.
Sequential diagonalizations of the sphere Hamiltonian, in the absence of the Rydberg ion core, yield the well-image energy levels of the nanoparticle as a function of sphere radius, as shown by the black lines in Figure 2. The Rydberg energies shown in red are determined using equation (7), where the energy of a Stark state $E_{nm,k}^{\text{Stark}}(F)$, in the presence of an electric field $F$ and at an atom-surface separation $D$ is approximated by [22],

$$E_{nm,k}(F, D) \approx E_{nm,k}^{\text{Stark}}(F) = \frac{n^2}{64D^3}(8n^2 + 8 - 4m^2 + 12k^2).$$  

The red lines are calculated for a Rydberg atom at $D = 3n^2$ from the nanoparticle. At the intersection of the black and red lines resonance-enhanced charge transfer is expected.

3.2. Ionization probability in the static-atom calculations

For bulk conducting materials, surface ionization is normally significant for surface-Rydberg atom distances less than $4n^2a_0$. The charge transfer is likely to be one-way because once the electron is transferred to the bulk metal it is dispersed amongst a continuum of states. However, the three-dimensional confinement of the nanoparticle potential means that a Rydberg atom held at a fixed position in front of a nanoparticle cannot be fully ionized. At these distances, the electron density of a static Rydberg atom near to a nanoparticle flows back and forth between localization on the Rydberg atom and localization on the nanoparticle, as the transfer is between one discrete state and another. In the near-resonant case this can be understood using a standard quantum treatment by considering the populations of a two-level system under the influence of a time independent perturbing potential $V_{\text{perturb}}(r, \theta) = V_{\text{total}}(r, \theta)$, where $\psi(0)$ is the initial wavefunction localized on the atomic core ($a_{\text{Ryd}}(0) \approx 1$),

$$\psi(t) = a_{\text{well}}(t)\psi_{\text{well}} + a_{\text{Ryd}}(t)\psi_{\text{Ryd}},$$

$$E_{\text{well}} - E_{\text{Ryd}} = \omega_0,$$

$$P_{\text{well}} = |a_{\text{well}}|^2 = \left(\frac{4V^2}{\omega_0^2 + 4V^2}\right) \sin^2 \frac{1}{2} \left(\frac{\omega_0^2 + 4V^2}{2}\right)t.$$
The surface ionization probability determined using a static-atom propagation for the $n = 2$ hydrogen atom Rydberg state and a nanoparticle of radius $R = 4\, a_0$ to $8\, a_0$. The red line shows the results from the static-atom propagations at an atom-surface separation $D = 16\, a_0$, and the black line at $D = 8\, a_0$. Note that the magnitude of the surface ionization probability for the $D = 16\, a_0$ propagations has increased three fold to aid comparison.

Here $V^2 = H_j^2$, where $i$ is the Rydberg state and $j$ is the well-image state, and equation (10) is the Rabi formula. $P_\text{well}$ is the probability of the electron occupying the nanoparticle well-image state as a function of time. The mathematical form shows that the probability of the electron being within the nanoparticle will oscillate in time sinusoidally and has an amplitude which, for small $V$, is inversely proportional to the squared energy gap between nanoparticle and Rydberg states, and a frequency which is linearly proportional (for small $V$) to the same gap. This is seen in the probability oscillations from the wavepacket propagation calculations where the oscillations for non-degenerate states that are close in energy are characterized by large amplitudes and low frequencies, and the larger the energy gap between the states the higher the frequency and the lower the amplitude. $P_\text{well}$ can be used as a measure of the surface ionization probability for a non-stationary state, by either determining the amplitude or frequency of the nanoparticle-localized population oscillation.

Static-atom calculations with the atom at a fixed position allow any resonance effects to be seen clearly without the complicating factor of a time-dependent wavepacket evolution on approach of the atom to the surface. In this work we artificially create a non-stationary state by determining the Rydberg wavefunction at a separation of $6\, a_0$ and then moving the atom instantaneously to a closer starting position where, because of the different surface potential, it is now in a non-stationary state. The measurement of a large amplitude and low frequency is indicative of a high probability of charge transfer, and in the following section the maximum amplitude of the population oscillation will be denoted as the surface-ionization (Rydberg to nanoparticle charge transfer) probability.

Figure 3 shows the surface ionization probability for the $n = 2$ hydrogen Rydberg atom held at a constant atom-surface separation, $D = 8\, a_0$ (black line), in front of a small nanoparticle of variable radius between $R = 4$ and $8\, a_0$. Clear resonance-enhancement of charge transfer is seen for a nanoparticle of radius $R = 4.7\, a_0$, $6.3\, a_0$, $7.6\, a_0$ and a low rate of charge transfer for a nanoparticle of radius $R = 4.3\, a_0$, $5.5\, a_0$, $7\, a_0$. The field-free and static-atom nature of these calculations means this variation with nanoparticle radius must be due to the energy matching between the Rydberg atom and the well-image state, i.e., at $R = 4.7\, a_0$, $6.3\, a_0$, $7.6\, a_0$ the well-image state and the $n = 2$ Rydberg atom are degenerate.

The red line in figure 3 depicts the static-atom wavepacket propagations carried out at $D = 4n^2 = 16\, a_0$. In this case the Rydberg atom is further from the nanoparticle, and has a much smaller probability of surface ionization than when it is held at $D = 2n^2 = 8\, a_0$. At smaller atom-surface separations, greater wavefunction overlap between the well-image state and the Rydberg state results in an increase in the rate of charge transfer. Also the distance $R$ at which resonance occurs is shifted as the Rydberg atom moves closer to the surface with these static-atom calculations showing resonance-enhanced charge transfer at $R = 5.3\, a_0$, $6.7\, a_0$, $7.5\, a_0$. This is because as the Rydberg atom approaches the surface its energy levels are raised relative to the nanoparticle states and so it is degenerate with a well-image state in a slightly different-sized nanoparticle.

Figure 2 depicts the energy level diagram for the $R = 5-10\, a_0$ nanoparticle at $D = 3n^2 = 12\, a_0$. It predicts resonance-enhancement for the $n = 2$ hydrogen atom incident at an $R = 6.7$ or $7.8\, a_0$ radius nanoparticle, which is slightly different from the maxima seen in figure 3. This is because figure 2 omits the presence of the ion core in the calculation of nanoparticle well-image states, and also because it predicts the energy shift for a Rydberg atom approaching a flat metal surface, rather than for a Rydberg atom approaching a nanoparticle. Additionally the energy level diagram will change with atom-surface separation. However the spacings between resonances and the number of resonances match well.

3.3. The effect of the nanoparticle dimensions on the surface ionization probability

The low density of states in a sphere of small radius gives a clear picture of the resonance-enhancement of charge transfer, but in reality the particles would be clusters of atoms just a few atoms wide, so it is desirable to carry out wavepacket propagations at larger radii, in the nanometer range. This presents a theoretical challenge, as the DVR grids [23] required to model such a system are much larger, and so converging the results becomes computationally much more challenging.

Diagonalizations have been carried out on spheres of radius up to $R = 3\, \text{nm}$ in the absence of the Rydberg atom to show the density of states as a function of sphere radius (upper panel of figure 4). The calculated surface ionization probability for a $n = 2$ hydrogen atom Rydberg state incident at a nanoparticle of $R \approx 1\, \text{nm}$ (determined as described above) is shown in the lower panel of figure 4. The energy level diagram predicts three resonances as the radius is tuned, and three peaks are seen in the calculated surface ionization
probability. All are slightly shifted due to the change in Rydberg energy as the atom moves closer to the nanoparticle. While the nanoparticle radius stepsize used for figure 4 is sufficient to demonstrate the occurrence of resonances and is less than the achievable experimental precision, the resonances are likely to be narrower than suggested by figure 4.

As shown in figure 5, additional static-atom propagations have been carried out in the absence of a field for jellium spheres in the range of $R = 1\,\text{nm}$, $R = 2\,\text{nm}$ and $R = 3\,\text{nm}$. In this size range it is still possible to see resonance-enhanced charge transfer due to the degeneracy of an individual nanoparticle well-image state and the Rydberg atom. However it is also clear that for this to be experimentally measurable, the dimensions of any sample of nanoparticles must be uniform and very well defined, perhaps to a precision ($\sim 0.1\,\text{nm}$) that is not currently achievable experimentally. Thus from an experimental perspective, resonance enhancement is most likely to be observed by measuring surface-ionization probability as a function of principal quantum number (and hence the Rydberg orbital radius) rather than nanoparticle radius. To observe resonance effects it would be essential to tailor the range of Rydberg states populated such that the energy density of the Rydberg states is higher than that of the nanoparticles. As can be seen from figure 2, in the situation where the size of the nanoparticle and Rydberg atom are comparable, the density of the well-image states in the nanoparticle and the density of the H-atom Rydberg states are comparable. Therefore it is expected that for larger nanoparticles $>1\,\text{nm}$ radius, resonance effects would be measurable, but only for higher principal quantum number Rydberg atoms. Using $r = n^2a_0$ for the Rydberg radius, a $1\,\text{nm}$ radius nanoparticle would be of comparable dimensions to an $n = 4$ or $5$ Rydberg atom, while a $10\,\text{nm}$ nanoparticle would correspond in size to a $n = 13$ Rydberg atom. These principal quantum numbers should be considered as a lower limit for the range of Rydberg states that should be employed.

3.4. Dynamic-atom calculations

The static-atom calculations are useful for elucidating pure resonant effects; but the idea of holding a Rydberg atom at a fixed atom-surface separation, where significant surface ionization is occurring, is clearly unphysical. In the Rydberg surface ionization experiments performed to date, the Rydberg atom has a velocity towards the surface which can have a significant effect on the resultant surface ionization dynamics [8, 9].

Once the Rydberg atom is given a non-zero velocity, the perturbing surface potential evolves in time, because the magnitude of its constituent parts is dependent on the atom-surface separation, $D$. The result is that the system no longer forms an oscillating non-stationary state in the same sense as the static-atom calculations. In the time interval when the electron density is initially building up in the nanoparticle state, the coupling perturbation and hence the energy of the Rydberg atom changes as it approaches the surface, such that resonance-enhancement will be optimal at a specific atom-surface separation. Thus as the Rydberg atom continues towards the surface it will move out of resonance with the well-image state, and hence the flow of electron density back into the Rydberg atom will be minimal. In effect, in the probability. All are slightly shifted due to the change in Rydberg energy as the atom moves closer to the nanoparticle. While the nanoparticle radius stepsize used for figure 4 is sufficient to demonstrate the occurrence of resonances and is

Figure 4. The energy level diagram (upper panel) and the surface ionization probability (lower panel) of the $n = 2$ hydrogen atom Rydberg state and a $R \approx 1\,\text{nm}$ nanoparticle calculated using a static wavepacket propagation. The arrows indicate the matching between the predicted resonances from the diagonalizations, and the positions of resonance-enhanced charge transfer from the surface ionization probabilities.

Figure 5. The surface ionization probability for an $n = 2$ hydrogen Rydberg atom near a nanoparticle with a variable radius around 1, 2 and 3 nm calculated using a static propagation method.
dynamic simulations actual surface ionization (i.e. irreversible electron transfer) can be seen.

Figure 6 shows the surface ionization probability (black line) for the \( n = 2 \) H atom Rydberg state incident at small nanoparticles of a various selected sizes. The dynamic calculations were all carried out at \( v_1 = 656 \text{ m s}^{-1} \). Similar to previous wavepacket propagation studies at conducting metal and projected-band-gap surfaces, the surface ionization probability is given by the flux of electron density into the surface, or in this case the jellium sphere \([2, 8]\). The red lines in figure 6 depict the fraction of the electron localized on the atom, such that a value of 1 indicates no surface ionization, and a value of 0 represents full surface ionization. In our previous projected-band-gap study with a Cu(111) surface, the maximum value of the surface ionization probability was observed at a much larger atom-surface separation when there was a resonance between the surface localized state and the Rydberg atom \([8]\), than for off-resonant principal quantum numbers. This results in more surface ionization being detectable experimentally through the extraction of the ions in an applied field. In the nanoparticle case, unlike the projected band gap surface case, there are no higher angular momentum (parallel momentum) states in the background metallic continuum, and so when the Rydberg atom is off-resonance with the nanoparticle the electron density cannot penetrate into the nanoparticle at all. Ultimately, at very short distances, the Rydberg atom and the nanoparticle will collide and the calculations presented here are not able to reliably model that situation.

Figure 7 shows the total surface-ionization probability, calculated by taking the integral of the surface ionization probability over all atom-surface separations. Resonance-enhanced charge transfer is seen at \( R = 6.5a_0, 8a_0, \) and \( 9.5a_0 \). The same size-range of nanoparticles is used in these dynamic calculations as in the static-atom calculations, hence figure 7 is directly comparable with figure 3. However resonance-enhanced charge transfer from the \( n = 2 \) hydrogen atom Rydberg state to the nanoparticle occurs at slightly different radii for the two sets of calculations. This is due to the shift in the energy of the Rydberg atom as it approaches the nanoparticle. The situation in the dynamic case is complex, as the Rydberg energy changes with atom-surface separation such that at different times in the wavepacket evolution the energy gap between the Rydberg and the well-image state is different. The atom-surface separation tunes the hydrogen Rydberg atom energy, and the nanoparticle radius tunes the well-image state energy, such that resonance-enhanced charge transfer can occur for different sized nanoparticles at different atom-surface separations. However ultimately this effect is limited, as the energy...
shift on approaching a surface is small, and the greater the atom-surface separation required for optimal energetic overlap, the worse is the overlap of spatial wavefunctions.

Figure 8 depicts the surface ionization probability and fraction of electron density on the Rydberg atom for a $n = 2$ hydrogen atom incident at a small nanoparticle of approximately 0.5 nm radius. The radius is tuned in steps of $0.1a_0$ to show the evolution of a resonance with radius, and therefore with the nanoparticle well-image state energy. The increased surface ionization probability, at larger atom-surface separations, for the $R = 9.4a_0$ nanoparticle is due to the better energy matching of the Rydberg state and the well-image state, than in the other propagations.

3.5. Potential for experimental measurement

Figure 10 shows the energy level diagram for H atom Rydberg states, $n = 26–34$, the range which has been experimentally accessed in previous work, and for nanoparticles of 3 viable sizes. Experimentally, instead of tuning the radius of an individual nanoparticle, a range of different principal quantum numbers could be used for the Rydberg atoms scattered from the same nanoparticle surface, as discussed above. These calculations predict no resonant principal quantum numbers in the $R = 0.5$ nm case; $n = 33, 26$ are near-resonant when incident at a surface of $R = 1$ nm nanoparticle and $n = 34, 31, 27$ are near-resonant at the $R = 1$ nm nanoparticle surface.

In previous experiments, the Rydberg atom—surface resonant charge transfer process has been measured by

Like in the static-atom case, the nanoparticles investigated so far using dynamic wavepacket propagations have been too small to be experimentally viable as spherical particles. Therefore dynamic propagations were also carried out with a $n = 2$ atom incident at series of nanoparticles with diameters on the nanoscale, as shown in figure 9. The $R = 1, 1.5, 2.5, 3$ nm propagations all show resonance-enhanced charge transfer at $D = 3.8n^2$ and full surface ionization of the electron wavepacket. However the $n = 2$ Rydberg atoms incident at the $R = 0.5$ nm nanoparticle show a lower rate of surface ionization at distances where the particles of other radii show a maximum rate. This suggests that the discrete nature of the energy states is more prominent at this size (the Rydberg radius is ca 0.2 nm) and the energy level separation has increased to a degree where there is more ‘off-resonant’ character to the nanoparticle—Rydberg atom interaction.
extracting the ions produced during surface ionization, via the application of a large external field. The results in this paper are intended to show that such a method could be used to measure charge transfer from a Rydberg atom to a nanoparticle. As the reverse process of charge transfer from the surface to the ion core results in neutral hydrogen atoms, it would be more difficult to investigate such a process experimentally and therefore has not been investigated theoretically here.

It is well known that metallic nanoparticles also show surface plasmon resonances that vary in frequency with the particle diameter. The current calculations are unable to probe whether the existence of such resonances would affect the charge transfer from a Rydberg atom because the plasmon resonances are collective oscillations of valence electrons that would not be predicted in these one-electron calculations.

The $n = 26–34$ hydrogen Rydberg atoms have been shown previously to resonantly charge transfer with well-image states in thin metallic films [10]. The higher energies of these Rydberg atoms would allow us to probe a region of the nanoparticles’ surface electronic structure where there is a lower density of well-image states and the states have more image-state character. Therefore it is expected that resonant charge transfer between a Rydberg atom and a nanoparticle should be experimentally measurable.

### 4. Conclusions and future perspectives

The calculations presented in this paper show resonance-enhanced charge transfer between a hydrogen Rydberg atom and a degenerate well-image state in a nanoparticle. Diagonalizations show that as the nanoparticle increases in size, its well-image states become closer together in energy, and have greater well-state character. Ultimately with infinite radius, the limit of a flat metallic surface is reached. Due to the computational expense of the wavepacket propagation calculations involving a confined potential, the calculations presented here are limited to $n = 2$ hydrogen Rydberg atoms and small nanoparticles. However it is expected that the predicted effects will occur in larger nanoparticles and for the experimentally accessible range of Rydberg atom principal quantum numbers i.e. those with sufficient lifetimes to perform the scattering experiments.

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**Figure 10.** Energy level diagrams for a nanoparticle (black lines) of $R = 0.5$, 1, 1.5 nm with the experimentally accessible $n = 26–34$ Rydberg energy levels (red lines) calculated from equation (7).