

Rydberg Electron Interferometry

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A recent quantum mechanical study [W. Isaacs and M. A. Morrison, *Phys. Rev. A* **57**, R9 (1998)] discovered pronounced oscillations in cross sections for near-resonant energy transfer collisions of rare-gas atoms with initially aligned Rydberg atoms. We analyze such collisions for $17d_m \rightarrow 18p_{m'}$ transitions in the Ca-He system semiclassically and show that the oscillations arise from a phase interference process unique to Rydberg target states. In addition to explaining the origin of these structures, this analysis explains their disappearance when the relative Ca-He velocity goes to infinity and/or the energy defect vanishes and their dependence on the initial and final magnetic quantum numbers of the transition.

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Recent experimental and theoretical investigations discovered the unexpected presence of pronounced alignment effects in cross sections for near-resonant energy transfer collisions of rare-gas atoms with Rydberg atoms. In these studies, the initial state of the Rydberg electron is aligned (e.g., via multiple pulsed-laser excitation) and inelastic cross sections are analyzed for effects such as a dependence on the angle between the polarization of the exciting laser and the relative velocity of the rare-gas projectile [1–3]. Such effects signal that the excited electron “remembers” its initial alignment through the collision. Studies of alignment phenomena have generated great interest because of the detailed insight they provide into fundamental mechanisms that influence the dynamics and properties of colliding particles [4–6].

Nearly all previous investigations of alignment in near-resonant energy transfer collisions have considered targets in *low-lying* excited states, not Rydberg states. For such targets, the qualitative explanation of alignment effects has been predicted on the formation during the collision of a transient quasimolecular electronic state. According to these “orbital following” and “locking” models [4,7,8], the orbital of the excited electron temporarily couples to the internuclear axis of the quasimolecule. Consequently, depending on the distance at which the orbital “locks” and the symmetry of the resulting electronic state, cross sections may exhibit alignment effects of varying degree.

Such models, however, are not germane to collisions with *Rydberg* atoms, where the electron’s comparatively low speed and extremely diffuse probability density invalidate a molecular (Born-Oppenheimer) description of the dynamics [9,10]. Hence cross sections for rare-gas collisions with *Rydberg* atoms were not expected to manifest alignment effects. Nevertheless, measurements by Spain *et al.* [11] revealed unambiguous effects in cross sections for the $17d \rightarrow 18p$ transition in Ca resulting from collisions with ground-state Xe atoms at a single mean relative velocity. Quantum calculations by Isaacs and Morrison [12,13] confirmed these results and, by exploring a wide range of relative velocities, uncovered

hitherto unknown oscillatory structures in the cross sections for this transition (see Fig. 1). The assumptions of these calculations explicitly precluded the formation of a quasimolecular state, so the origin of the alignment effects, the oscillations, and their striking dependence on the initial and final magnetic quantum numbers of the electron all remained a mystery.

In the present Letter we use a semiclassical time-dependent analysis [14–17] to uncover the physical mechanism behind these structures. Specifically, we interpret the oscillations as a type of quantum mechanical interference heretofore unknown in Rydberg collisions.

The most straightforward way to study alignment effects theoretically is to first calculate state-to-state cross sections for the transitions $\alpha = (n, \ell, m) \rightarrow \alpha' = (n', \ell', m')$ for all magnetic quantum numbers m and m' allowed by the orbital angular momentum quantum numbers ℓ and ℓ' of the excitation $(n, \ell) \rightarrow (n', \ell')$. One then sums the

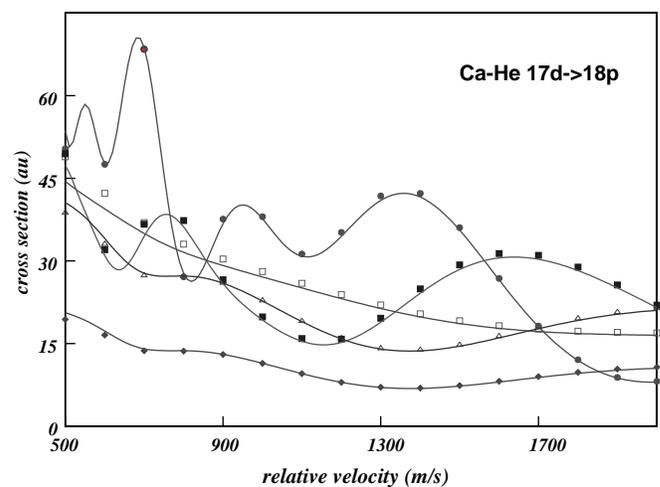


FIG. 1. State-to-state cross sections for $17d_m \rightarrow 18p_{m'}$ transitions in Ca-He collisions from quantal (solid curves) and semiclassical (points) calculations: $0 \rightarrow 0$ (closed circles), $1 \rightarrow 1$ (open triangles), $2 \rightarrow 1$ (open squares), $1 \rightarrow 0$ (closed squares), and $2 \rightarrow 0$ (closed diamonds).

resulting cross sections over final state m' for each initial m . The extent to which each of the resulting partial cross sections $\sigma^{|m|}(v)$ depend on $|m|$ at a particular relative velocity v is a measure of the strength of the alignment effect: if these quantities are independent of $|m|$, then no such effects are present and the collision has obliterated all information concerning the initial alignment of the Rydberg electron [18].

We calculate state-to-state cross sections by solving the time-dependent Schrödinger equation of the Rydberg electron in a semiclassical approximation in which the rare-gas projectile is treated as a point particle moving along a straight-line trajectory through the quantum mechanical probability density of the Rydberg electron. (The latter assumption is based on the mass difference between the projectile and the electron. Examination of differential cross sections from quantal calculations [12] show this assumption to be extremely accurate for the system considered here.) The singly charged core of the Rydberg atom plays no direct role in the collision; this “spectator” merely supports the initial and final bound states of the electron. Hence in this widely used “quasi-free-electron model,” [9,19,20] quasimolecular state formation cannot occur; the transition results essentially from the collision of a very weakly bound electron with the rare-gas projectile.

The time-dependent interaction between these two particles is represented by the Fermi contact potential

$$\hat{V}(t) = 2\pi A \left(\frac{\hbar^2}{m_e} \right) \delta(\mathbf{r} - \mathbf{R}), \quad (1)$$

where A is the effective scattering length for collisions of the rare-gas atom with the electron of mass m_e . This potential is zero except when the atom’s position \mathbf{R} coincides with the Rydberg electron’s coordinate \mathbf{r} , at which time the electron may undergo a (high nonadiabatic) transition. The Fermi potential does not include the Rydberg electron–rare-gas polarization interaction; rather, it assumes that the electron scattering amplitude for this very-low-energy collision may be approximated by [21] $f^{(e)} \approx -A$. Polarization effects do influence the magnitude (though not the structure) of Ca-Xe cross sections, so we here consider Ca-He scattering—for which neglect of polarization is an excellent approximation in the relevant energy range. Quantal calculations show that Ca-He cross sections manifest effects comparable in magnitude and structure to those in Ca-Xe scattering [12].

Considering a two-state model, we write the wave function of the Rydberg electron in terms of time-dependent transition amplitudes $a_\alpha(t)$ as

$$\Psi(\mathbf{r}, t) = a_\alpha(t) e^{-iE_\alpha t/\hbar} \psi_\alpha(\mathbf{r}) + a_{\alpha'}(t) e^{-iE_{\alpha'} t/\hbar} \psi_{\alpha'}(\mathbf{r}). \quad (2)$$

We represent the stationary-state eigenfunctions $\psi_\alpha(\mathbf{r})$ of the Rydberg electron by products of phase-shifted hydrogenic radial functions and spherical harmonics. The for-

mer are shifted [22] by the quantum defects of the relevant states (for Ca, $\delta_{17d} = 0.9043$ and $\delta_{18p} = 1.8721$). The corresponding energies, which in atomic units are given by $\epsilon_{n\ell} = -1/[2(n - \delta_{n\ell})^2]$, are 428.56 cm^{-1} for the $17d$ state and 421.89 cm^{-1} for $18p$, giving an energy defect $\Delta\epsilon \equiv E_{\alpha'} - E_\alpha$ of 1.69 cm^{-1} . Initially, the electron is in state α , so $a_\alpha(t \rightarrow -\infty) = 1$ and $a_{\alpha'}(t \rightarrow -\infty) = 0$.

For the wave function (2), the final-state transition amplitude is

$$a_{\alpha'}(t) = -\frac{i}{\hbar} \int_{-\infty}^t a_\alpha(t') e^{i\Delta\epsilon t'/\hbar} \langle \alpha' | \hat{V}(t') | \alpha \rangle dt'. \quad (3)$$

The Fermi potential reduces the transition matrix element $\langle \alpha' | \hat{V}(t') | \alpha \rangle$ to a number proportional to the *transition density* $\mathcal{P}_{\alpha',\alpha}(\mathbf{r}) \equiv \psi_{\alpha'}^*(\mathbf{r}) \psi_\alpha(\mathbf{r})$ evaluated at $\mathbf{r} = \mathbf{R}(t')$. To first order, the transition amplitude becomes

$$a_{\alpha'}(t) = -i(2\pi A) \left(\frac{\hbar}{m_e} \right) \int_{-\infty}^t e^{i\Delta\epsilon t'/\hbar} \mathcal{P}_{\alpha',\alpha}(\mathbf{R}(t')) dt'. \quad (4)$$

The squared modulus of this quantity in the $t \rightarrow +\infty$ limit is the first-order transition probability $P_{\alpha \rightarrow \alpha'}$.

In a reference frame fixed on the spectator core with z axis parallel to the rare-gas velocity \mathbf{v} , the trajectory of the projectile can be written in terms of impact parameter b and unit vectors \mathbf{e}_x and \mathbf{e}_z as $\mathbf{R}(t) = b\mathbf{e}_x + vt\mathbf{e}_z$, where we have exploited the axial symmetry of the system to set $\varphi = 0$. Using cylindrical coordinates $[b, \varphi, z(t)]$, the transition probability can be expressed as an integral over $z = vt$ as

$$P_{\alpha \rightarrow \alpha'}(v; b) = \left(\frac{2\pi A \hbar}{m_e} \right)^2 \frac{1}{v^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i\Delta\epsilon(z-z')/(\hbar v)} \times \mathcal{P}_{\alpha',\alpha}(z, b) \mathcal{P}_{\alpha',\alpha}(z', b) dz dz', \quad (5)$$

where we have used the fact that $\mathcal{P}_{\alpha',\alpha} = \mathcal{P}_{\alpha,\alpha'}$ is real and independent of the azimuthal angle φ . The sine functions in the phase of the integrand average to zero upon integration over z and z' , leaving

$$P_{\alpha \rightarrow \alpha'}(v; b) = \left(\frac{2\pi A \hbar}{m_e} \right)^2 \frac{1}{v^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \cos \left[\frac{\Delta\epsilon}{\hbar v} (z - z') \right] \times \mathcal{P}_{\alpha',\alpha}(z, b) \mathcal{P}_{\alpha',\alpha}(z', b) dz dz'. \quad (6)$$

The state-to-state cross section accumulates transition probability over all impact parameters,

$$\sigma_{\alpha \rightarrow \alpha'}(v) = 2\pi \int_0^{\infty} P_{\alpha \rightarrow \alpha'}(v; b) b db. \quad (7)$$

Figure 1 shows these cross sections for several $m \rightarrow m'$ combinations. The $0 \rightarrow 0$ results manifest the most pronounced oscillations, while $\sigma_{2 \rightarrow 1}$ varies smoothly with v . The close agreement between quantal and semiclassical data validates the semiclassical picture underlying the present analysis. In this picture Eq. (6) explains the oscillations as phase interference phenomena resulting from the spatial distribution of Rydberg electron wave functions. The initial and final radial functions associate certain regions of space with electron probabilities that are

higher than those in adjacent regions. As modulated by angular factors in the transition density $\mathcal{P}_{\alpha',\alpha}(z, b)$, these high-probability regions demarcate space in ways that depend strikingly on m and m' . To illustrate, Fig. 2 shows transition densities for the two extreme cases, the transitions $m = 0 \rightarrow m' = 0$ and $2 \rightarrow 1$. Because the radial dependencies of these densities are identical, they differ only in the angular factors, which, in turn, depend on m and m' . If a rare gas atom with impact parameter b encounters regions at z and z' at both of which the transition densities are comparatively large, this encounter will contribute significantly to the transition probability (6). In effect, the factors $\mathcal{P}_{\alpha',\alpha}(z, b)$ and $\mathcal{P}_{\alpha',\alpha}(z', b)$ at these values of z and z' represent two “opportunities” or “paths” whereby the Rydberg electron can be excited to state α' . As v varies, the cosine factor in (6) induces interference oscillations between the two highly nonadiabatic interactions at z and z' . This interference disappears as $\Delta\epsilon \rightarrow 0$ or $v \rightarrow \infty$, and otherwise produces peaks spaced as v^{-1} —all properties observed in the cross sections in Fig. 1. While integration over impact parameter in Eq. (7) smooths these features, it does not alter the qualitative predictions of Eq. (6).

To clarify the origin of the oscillations, we consider the extreme model of a Rydberg state in which the electron presents to the rare gas atom only two “planes” of transition density, one at z_1 and one at z_2 , i.e.,

$$\mathcal{P}_{\alpha',\alpha}(\mathbf{R}(t)) = \psi_{\alpha'}^*(\mathbf{R}(t))\psi_{\alpha}^*(\mathbf{R}(t)) \times \{\delta[z(t) - z_1] + \delta[z(t) - z_2]\}. \quad (8)$$

Since in this model transitions can occur at either interaction time t_1 or t_2 such that $z(t_1) = z_1$ and $z(t_2) = z_2$, the transition probability (5) reduces to

$$P_{\alpha \rightarrow \alpha'}(v; b) = \left(\frac{2\pi A\hbar}{m_e}\right)^2 \frac{1}{v^2} \left\{ \mathcal{P}_{\alpha',\alpha}^2(b, z_1) + \mathcal{P}_{\alpha',\alpha}^2(b, z_2) + 2 \cos\left[\frac{\Delta\epsilon}{\hbar v}(z_2 - z_1)\right] \mathcal{P}_{\alpha',\alpha}(z_1, b)\mathcal{P}_{\alpha',\alpha}(z_2, b) \right\}. \quad (9)$$

All three appearances of the transition density in this result participate in the m and m' dependence of the resulting cross sections. Extensive tests (not shown) demonstrated that, provided z_1 and z_2 are far enough apart ($\Delta z \gtrsim 150a_0$), their particular values do not matter. For $0 \rightarrow 0$ one can easily find planes which induce oscillations in $\sigma_{0 \rightarrow 0}$, while for $2 \rightarrow 1$ there are no planes which cause structure in $\sigma_{2 \rightarrow 1}$. The variations in Fig. 1 with v and with m and m' of cross sections determined from the actual transition densities of Fig. 2 reflect the more distributed nature of these densities as compared with this two-plane model.

Unlike the quantal impulse formulation of Ref. [13], the present semiclassical theory clearly reveals that oscillatory alignment effects in near-resonant energy transfer collisions of rare-gas atoms with aligned Rydberg atoms originate in quintessentially quantum mechanical interference—specifically, between multiple “paths” by which the

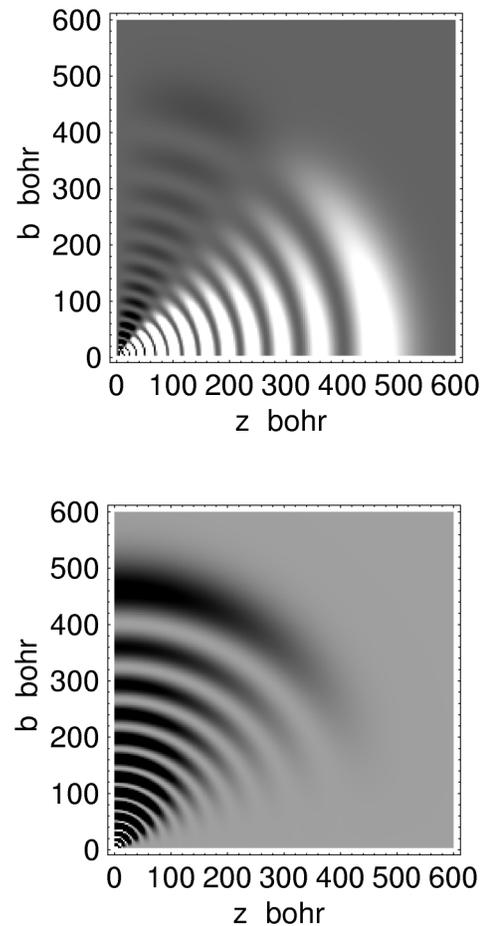


FIG. 2. Density plots of transition densities for the $0 \rightarrow 0$ (upper) and $2 \rightarrow 1$ (lower) state-to-state $17d_m \rightarrow 18p_{m'}$ transitions in Ca-He collisions. Light regions correspond to large values, dark to small values.

projectile may induce a transition in the Rydberg electron. This analysis further suggests that angular momentum phase interference may also play a role in collisions involving aligned *low-lying* excited target states—as seen, for example, in measured and calculated results for the process [23] $\text{Ca}^{**}(4s4f^1F) + \text{He} \rightarrow \text{Ca}^{**}(4p^2^1S) + \text{He}$. Partial cross sections for this transition show structures quite similar to those in Fig. 1: σ^0 manifest pronounced oscillations, those in σ^1 are weaker, and σ^2 and σ^3 vary smoothly with v . This behavior may arise from simple angular momentum considerations rather than the more complicated orbital locking mechanisms thus far proposed. We hope the present findings will stimulate further experimental and theoretical investigation of Rydberg electron interference.

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