

Coherent Control of Penning and Associative Ionization: Insights from Symmetries

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Coherent control of reactive atomic and molecular collision processes remains elusive experimentally due to quantum interference-based requirements. Here, with insights from symmetry conditions, a viable method for controlling Penning and associative ionization in atomic collisions is proposed. Computational applications to $\text{He}^*(^3S)\text{-Li}(^2S)$ and $\text{Ne}^*(^3P_2)\text{-Ar}(^1S_0)$ show extensive control over the ionization processes under experimentally feasible conditions.

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Coherent control makes use of the quantum interference of different pathways to control the outcome of a physical process [1]. As a quantum interference effect it is exquisitely sensitive to the requirement of pathway indistinguishability. This condition presents a major challenge for the control of bimolecular collisions, which requires entanglement of internal vibrational and external translational degrees of freedom for quantum interference to occur [2–5]. However, there are two classes of processes for which these obstacles were conceptually overcome: the tetra-atomic reaction $AB + AB \rightarrow A_2 + B_2$ [1,4], as well as Penning (PI) and associative ionization (AI) [6,7]. (An overview of these issues is provided in chapter 8 of Ref. [1].)

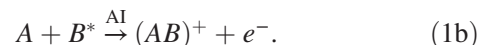
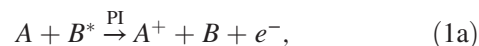
The control of PI and AI is extremely important in, e.g., the formation of Bose-Einstein condensates, since the ionization leads to losses in the trap [8]. PI and AI are also important in the spectroscopy of surfaces [9], plasma chemistry [10,11], or atmospheric studies [12]. Similarly, control of the $AB + AB$ reaction would eliminate undesired chemical processes in ultracold gases [13].

Although bond making has been demonstrated [14,15], to date there has been no experimental demonstration of quantum interference controlled reactive collisional processes. However, experimental technology in the control and study of interatomic collisions has seen tremendous progress in recent years. In particular, advances in the control of ultracold atoms and molecules allows for a precise preparation and investigation of different collision scenarios [16–19]—including PI at 10 mK [20]. In addition, the use of additional optical and static fields enables one to study the stereodynamics of the collisional processes [21]. Very recently this ansatz has been used to obtain the branching ratio of PI and AI in the collision of $\text{Ne}^*(^3P_2) + \text{Ar}(^1S)$, Kr, Xe, and N_2 [22,23,24], resolved for different initial incident angles. In light of these recent developments in experimental techniques and the absence of experimental demonstrations of collisional control,

a reexamination of coherent control approaches in collisional processes is strongly motivated.

This Letter provides a viable method for the coherent control of Penning and associative ionization as an example of the interference-based control of collisional processes. In addition to doing so we also resolve crucial symmetry issues that were inadvertently neglected in prior work [6,7]. Resolving these issues also offers considerable insight into conditions for interference in angular momentum controlled processes of interest here.

In Penning and associative ionization (reviewed in Ref. [25]) two atoms A and B collide—with at least one (here B) being initially in a metastable state B^* —, leading to ionization:



In the Penning mechanism, the metastable species B^* relaxes to its ground state while the other atom becomes ionized. In AI, on the other hand, an ionic dimer $(AB)^+$ is formed. In both cases an electron is ejected. In general, PI and AI can decay to the same molecular channel, where a bound (AI) or a continuum state (PI) is formed.

The initial state of the colliding atoms may be written as a product [7]

$$|\psi\rangle = |\psi_A\rangle|\psi_B\rangle, \quad (2)$$

where $|\psi_A\rangle$ and $|\psi_B\rangle$ are the initial states of the atom A and B , which, in the laboratory fixed frame (LFF), are

$$|\psi_A\rangle = \exp(i\vec{k}_A\vec{r}_A) \sum_n a_n |\phi_A^n\rangle, \quad (3)$$

$$|\psi_B\rangle = \exp(i\vec{k}_B\vec{r}_B) \sum_m b_m |\phi_B^m\rangle. \quad (4)$$

Here, $\vec{k}_X$ and $\vec{r}_X$ denote the linear momentum and position of atom X , and the sum on the right-hand side is its electronic state. Note that the latter is a superposition of electronic eigenstates $|\phi_X^i\rangle$ with expansion coefficients a_i, b_i . For convenience, we introduce the center of mass $\vec{R}$ and the internuclear separation vector $\vec{r}$ as coordinates:

$$\vec{R} \equiv \frac{m_A \vec{r}_A + m_B \vec{r}_B}{m_A + m_B}, \quad (5)$$

$$\vec{r} \equiv \vec{r}_B - \vec{r}_A, \quad (6)$$

where m_X is the mass of species X . The respective linear momenta are given by

$$\vec{K} \equiv \vec{k}_A + \vec{k}_B, \quad (7)$$

$$\vec{k} \equiv \frac{m_A \vec{k}_B - m_B \vec{k}_A}{m_A + m_B}. \quad (8)$$

Inserting expressions (5)–(8) into Eq. (2) yields

$$|\psi\rangle = \exp(i\vec{K}\vec{R} + i\vec{k}\vec{r}) \sum_{n,m} a_n b_m |\phi_A^n\rangle |\phi_{B^*}^m\rangle. \quad (9)$$

The total cross sections for PI and AI are given by

$$\sigma^{\text{PI/AI}}(\{c_S\}) = \sum_{S,S'} c_S^* c_{S'} \sigma_{S,S'}^{\text{PI/AI}}, \quad (10)$$

where we have introduced $S \equiv (n, m)$, $c_S \equiv a_n b_m$, and $|S\rangle \equiv |\phi_A^n\rangle |\phi_{B^*}^m\rangle$. Here $\sigma_{S,S'}^{\text{PI/AI}}$ is the cross section for PI or AI associated with an initial state which is a superposition of $|S\rangle = |\phi_A^n\rangle |\phi_{B^*}^m\rangle$ and $|S'\rangle = |\phi_A^{n'}\rangle |\phi_{B^*}^{m'}\rangle$. The terms $\sigma_{S,S'}^{\text{PI/AI}}$ can be obtained by integrating the differential cross sections over continuum and bound final states [7,26].

For the collision operator $\hat{W}$, the cross section into a specific exit channel $|f\rangle$ is given as [1]

$$\sigma_f = |\langle f | \hat{W} | \psi \rangle|^2 = \sum_{S,S'} c_S c_{S'}^* \langle f | \hat{W} | S \rangle \langle S' | \hat{W} | f \rangle. \quad (11)$$

From this expression we can compute the total cross section in Eq. (10) by summing over all the final channels $|f\rangle$. Interference is manifest in the cross terms $S \neq S'$ in σ_f [1] with control affected via the coefficients c_S . For example, changing the phases of c_S alters σ_f through the interference contribution.

For any symmetry that is conserved by $\hat{W}$, the cross terms are nonzero only if $|f\rangle$, $|S\rangle$, and $|S'\rangle$ are of the same symmetry [27]. For example, for the case of coherent control of collisional processes in the absence of an external, time-dependent field, the energy as a conserved quantity leads to the constraint that the initial state has to be

a linear superposition of energetically *degenerate* states. In past proposals for coherent control of the AI and PI cross sections, this constraint was taken into account by choosing a metastable state with nonzero angular momentum J , and using the degenerate states of different magnetic quantum number M_J to construct the superposition state [6,7]. However, as will be shown in the following, this may not be sufficient since we must also properly take into account the invariance of the collisional cross section under rotations in the LFF.

Specifically, in the absence of an external field, the collision process is invariant with respect to any rotation of the LFF. Consider then the collision between atoms A and B , and define the Z axis of the LFF by the directional vector of the relative momentum $\vec{k}$ at $t \rightarrow -\infty$. Furthermore, assume that the atoms A and B are initially in states with well-defined magnetic quantum numbers M_A and M_B , which are the projection of each atom's electronic angular momentum on the Z axis. The initial state then reads

$$|\psi\rangle = e^{(i\vec{K}\vec{R} + i\vec{k}\vec{r})\hat{Z}} |M_A\rangle |M_B\rangle. \quad (12)$$

For convenience we apply a boost to the center of mass frame (CMF), where $\vec{K} = 0$. In this frame, the wave function reads as

$$|\psi\rangle = e^{i\vec{k}\vec{r}\hat{Z}} |M_A\rangle |M_B\rangle. \quad (13)$$

Note that the total cross section is invariant with respect to a change of the reference frame [26]. Expression (13) does not depend on the azimuthal angle, φ , that is, the orbital magnetic quantum number is $M_N = 0$, so that, before the collision, the total magnetic quantum number of the $A-B^*$ system is $M_J = M_N + M_A + M_B = M_A + M_B$. Further, the Hamiltonian H commutes with rotations around any axis of the LFF, and in particular around the Z axis, i.e., $[H, \mathbf{J}_Z] = 0$. Thus $M_J = M_A + M_B$ is a good quantum number, implying that the final state, in the asymptotic limit $t \rightarrow \infty$, either for PI or AI, is also characterized by the same M_J . Therefore, two different initial states $|\psi\rangle$ and $|\psi'\rangle$ can decay to the same final state with magnetic quantum numbers M'_A, M'_B and hence interfere [1], only if $M_A + M_B = M'_A + M'_B$.

This restriction is intimately limited to the initial superposition state rotated around the LFF. Consider a more general initial state

$$|\psi\rangle = e^{i\vec{k}\vec{r}} |\psi_A\rangle |\psi_B\rangle, \quad (14)$$

where $|\psi_A\rangle = (a_1 |M_A^{(1)}\rangle + a_2 |M_A^{(2)}\rangle)$ and $|\psi_B\rangle = (b_1 |M_B^{(1)}\rangle + b_2 |M_B^{(2)}\rangle)$ are linear superpositions of magnetic quantum number states, with $M_A^{(1)} \neq M_A^{(2)}$ and $M_B^{(1)} \neq M_B^{(2)}$. Introducing the notation $c_{ij} \equiv a_i b_j$ and $|S_{ij}\rangle \equiv |M_A^{(i)}\rangle |M_B^{(j)}\rangle$, we can write

$$|\psi\rangle = e^{i\vec{k}\vec{r}}(c_{11}|S_{11}\rangle + c_{12}|S_{12}\rangle + c_{21}|S_{21}\rangle + c_{22}|S_{22}\rangle). \quad (15)$$

Using Eq. (10), the ionization cross section is given as

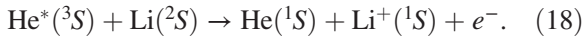
$$\begin{aligned} \sigma = & |c_{11}|^2\sigma_{11,11} + |c_{12}|^2\sigma_{12,12} + |c_{21}|^2\sigma_{21,21} + |c_{22}|^2\sigma_{22,22} \\ & + 2\text{Re}\{c_{11}^*c_{12}\sigma_{11,12} + c_{11}^*c_{21}\sigma_{11,21} + c_{11}^*c_{22}\sigma_{11,22} \\ & + c_{12}^*c_{21}\sigma_{12,21} + c_{12}^*c_{22}\sigma_{12,22} + c_{21}^*c_{22}\sigma_{21,22}\}. \end{aligned} \quad (16)$$

Now, apply a rotation $R(\gamma)$ around the Z axis of the LFF, which acts as $R(\gamma)e^{i\vec{k}\vec{r}}|M_A\rangle|M_B\rangle = e^{i\vec{k}\vec{r}}e^{i(M_A+M_B)\gamma}|M_A\rangle \times |M_B\rangle$. Using the notation $s_{ij} \equiv M_A^{(i)} + M_B^{(j)}$, the cross section for the rotated state, σ' , is

$$\begin{aligned} \sigma' = & |c_{11}|^2\sigma_{11,11} + |c_{12}|^2\sigma_{12,12} + |c_{21}|^2\sigma_{21,21} + |c_{22}|^2\sigma_{22,22} \\ & + 2\text{Re}\{c_{11}^*c_{12}e^{i(s_{12}-s_{11})\gamma}\sigma_{11,12} + c_{11}^*c_{21}e^{i(s_{21}-s_{11})\gamma}\sigma_{11,21} \\ & + c_{11}^*c_{22}e^{i(s_{22}-s_{11})\gamma}\sigma_{11,22} + c_{12}^*c_{21}e^{i(s_{21}-s_{12})\gamma}\sigma_{12,21} \\ & + c_{12}^*c_{22}e^{i(s_{22}-s_{12})\gamma}\sigma_{12,22} + c_{21}^*c_{22}e^{i(s_{22}-s_{21})\gamma}\sigma_{21,22}\}. \end{aligned} \quad (17)$$

Since a rotation of the LFF must not affect the total cross section, $\sigma = \sigma'$ has to hold for all angles γ . This can only be fulfilled if $\sigma_{ij,kl} = 0$ for all $s_{ij} \neq s_{kl}$. Thus, the only nonzero cross terms $\sigma_{ij,kl}$ that can give rise to quantum interference are those with for $M_A^{(1)} + M_B^{(1)} = M_A^{(2)} + M_B^{(2)}$, which is the same condition on the conservation of the total magnetic quantum number stated above. Note that this condition is based on symmetry operations in the LFF, and is independent of the interaction between the atoms. It is therefore generic for any bimolecular collision using degenerate magnetic states for coherent control. This rotational symmetry perspective allows a simple principle to aid in formulating effective control scenarios. Specifically, any coherent control scenario must rely on initial states that are anisotropic with respect to rotations in the LFF.

Consider as an example PI of metastable helium and lithium [28,29] (the AI cross section is here ignorable since HeLi^+ is very weakly bound [29]):



Since both atoms have an orbital angular momentum of zero, one need only be concerned with the electronic spin. There are six spin states $|S, M_S\rangle_m$, where $S = \frac{1}{2}, \frac{3}{2}$ is the total spin of the diatomic complex and $M_S = S, S-1, \dots, -S$ is its projection onto the Z axis (the direction of the relative momentum), and the subscript m denotes this as the molecular basis. The states with a total spin of $S = \frac{3}{2}$ form the quartet $^4\Sigma$, the states with a total spin of $S = \frac{1}{2}$ the doublet $^2\Sigma$.

Only the doublet states are autoionizing [29]. Thus it seems a logical choice to use a coherent superposition of the two doublet states for control:

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left|\frac{1}{2}, \frac{1}{2}\right\rangle_m + \frac{1}{\sqrt{2}}e^{i\beta}\left|\frac{1}{2}, -\frac{1}{2}\right\rangle_m, \quad (19)$$

where the cross section for PI from $|\frac{1}{2}, \frac{1}{2}\rangle_m$ is σ_+ and from $|\frac{1}{2}, -\frac{1}{2}\rangle_m$ is σ_- . However, in accordance with the discussion above, varying β will not provide control since the state is isotropic with respect to polarization in the LFF.

In addition, the state in Eq. (19) is likely hard to prepare experimentally. It is easier to create a superposition of the atomic states (both here and in the example below) by preparing the atoms prior to reaching the interaction zone, using established techniques such as electromagnetically induced transparency [30], coherent population trapping [31], or stimulated Raman adiabatic passage [32].

Consider then an initial state, with both atoms in a superposition of atomic states

$$|\Psi\rangle = \frac{1}{2}(|1, 1\rangle_{\text{He}} + |1, 0\rangle_{\text{He}})\left(\left|\frac{1}{2}, \frac{1}{2}\right\rangle_{\text{Li}} + e^{i\beta}\left|\frac{1}{2}, -\frac{1}{2}\right\rangle_{\text{Li}}\right). \quad (20)$$

The phase β for this state does not describe a rotation around the Z axis, and the ionization cross section becomes

$$\sigma = \left(\frac{1}{4} - \frac{1}{3\sqrt{2}}\cos\beta\right)\sigma_+ + \frac{1}{12}\sigma_-. \quad (21)$$

[This result is obtained by expressing the state (20) in the molecular basis.] Thus, by properly taking the symmetry of the collision process into account, coherent control of this bimolecular reaction becomes possible, through variations in the angle β .

The above process only includes one ionization channel. As a second example that includes both AI and PI consider $\text{Ne}^*(^3P_2) + \text{Ar}(^1S_0)$. This reaction was a prime focus in the proposed coherent control of a reactive bimolecular process [6,7], where $\text{Ne}^*(^3P_2)$ was initially in a superposition of Zeeman sublevels with projection $M_B^{(1)}$ and $M_B^{(2)}$ along the space fixed Z axis and the argon atom was in a single state with $M_A^{(1)} = 0$. Control was said to be achieved by varying the amplitude and phases of the $M_B^{(1)}, M_B^{(2)}$ superposition state. However, the overall state is symmetric with respect to rotation around the LFF Z axis. Hence, altering the phases and amplitudes of the $M_B^{(1)}$ and $M_B^{(2)}$ states on which the $\text{Ne}^*(^3P_2)$ superposition is comprised cannot, by the arguments above, result in control over the $\text{Ne}^*\text{-Ar}$ ionization process; that is, the control components of the computations in Refs. [6,7] were in error [33].

Consider, however, if the $\text{Ne}^*(^3P_2)$ state is comprised of a superposition of states that are quantized with respect to the X axis. Varying the relative phase between elements of the superposition would not correspond to a rotation in the LFF (in this basis the magnetic quantum number of the

nuclear orbital angular momentum is not zero) and control by tuning the phase becomes possible. Specifically, consider the initial state

$$|\Psi\rangle = |\text{Ar}\rangle \otimes (a_0|20\rangle_X + a_2|22\rangle_X), \quad (22)$$

where $a_0, a_2 \in \mathbb{C}$ and $|a_0|^2 + |a_2|^2 = 1$. Here $|2M\rangle_X$ is the electronic state of $\text{Ne}^*(^3P_2)$ with M being the magnetic quantum number along the X axis of the laboratory frame. In order to calculate the cross section, it is beneficial to use a Z -quantized basis, as this allows us to employ the rotating atom approximation [34]. The X -quantized states $|2M\rangle_X$ relate to the Z -quantized states $|2M\rangle$ by means of a $\pi/2$ rotation around the laboratory Y axis [35]

$$|2M\rangle_X = \sum_{M'=-2}^2 d_{M',M}^J(\pi/2) |2M'\rangle, \quad (23)$$

where $d_{M',M}^J(\theta)$ are the reduced Wigner matrix elements [35]. Substituting Eq. (23) in Eq. (22) we obtain

$$|\Psi\rangle = |\text{Ar}\rangle \otimes \left[\left(\sqrt{\frac{3}{8}}a_0 + \frac{a_2}{4} \right) (|22\rangle + |2-2\rangle) + \frac{a_2}{2} (|21\rangle + |2-1\rangle) + \left(\sqrt{\frac{3}{8}}a_2 - \frac{a_0}{2} \right) |20\rangle \right]. \quad (24)$$

Using the rotating atom approximation, the projection M of the angular momentum in the LFF is related to the projection Ω of the electronic angular momentum along the internuclear axis of the Ne-Ar dimer as $\Omega = |M|$. The cross sections σ_Ω for the three channels $\Omega = 0, 1, 2$ can now be calculated as described in Refs. [6,7]. For the reasons outlined above, there is no cross term between states of different M , and therefore also between different Ω , and thus the total cross section is given as

$$\sigma_\Psi^{\text{PI/AI}} = 2 \left| \sqrt{\frac{3}{8}}a_0 + \frac{a_2}{4} \right|^2 \sigma_2^{\text{PI/AI}} + \frac{|a_2|^2}{2} \sigma_1^{\text{PI/AI}} + \left| \sqrt{\frac{3}{8}}a_2 - \frac{a_0}{2} \right|^2 \sigma_0^{\text{PI/AI}}. \quad (25)$$

It is convenient to write a_0 and a_2 in terms of the Hopf coordinates in $\mathbb{C}^2$, such that $a_0 = \sin \eta$ and $a_2 = e^{i\xi} \cos \eta$, where $\eta \in [0, \pi]$ and $\xi \in [0, 2\pi)$. Note that thus η describes incoherent control via the population, and ξ coherent control via the relative phase. Typical results at 50 mK are shown in Fig. 1 and the cross sections σ_Ω for each Ω are collected in Table I. Evident is the extensive control of PI or AI as a function of η and ξ . For example, the cross section for AI can be varied by means of η and ξ from 400 to 1700 a.u., i.e., by a factor of over 4. (This control is reduced to a factor of 2 if one only tunes the relative phase ξ).

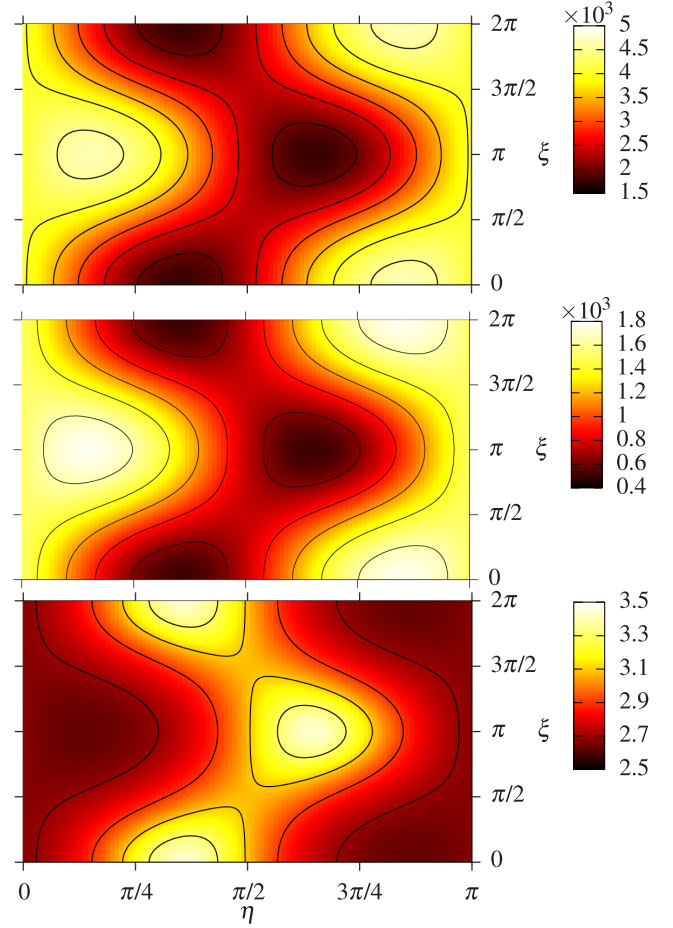


FIG. 1. Cross sections for AI (upper panel), PI (middle panel), and the ratio of the two (lower panel) in the $\text{Ne}^*\text{-Ar}$ system for the state (22), as a function of the control parameters η and ξ . The collision energy is 50 mK, and the cross sections are given in atomic units.

Similar results are shown for control of σ^{PI} . Interesting is that the functional dependence of σ^{AI} and σ^{PI} on η, ξ are similar, so that control over the ratio $\sigma^{\text{AI}}/\sigma^{\text{PI}}$ is not as extensive (from 2.5 to 3.5). Hence, one can control the total ionization by η and ξ , an important result, for example, for suppression of ionization in a Bose-Einstein condensate [8].

TABLE I. Cross sections σ_Ω for Penning (PI) and associative (AI) ionization in the $\text{Ne}^*\text{-Ar}$ system at $T = 50$ mK, for the three different values of the projection Ω of the electronic angular momentum onto the internuclear axis. Cross sections are given in atomic units.

Ω	σ^{PI}	σ^{AI}
0	1997.95	5223.49
1	1447.30	3850.76
2	350.73	1392.43

In summary, we have introduced a viable means of controlling, via quantum interference effects, both Penning and associative ionization in atomic collisions. Symmetry conditions were shown to provide insight into the selection of initial states for which control is possible. The axis of quantization along which superpositions of internal states is created was shown to be of particular importance in dictating the viability of control. In addition, significant control was demonstrated for two systems that are achievable with current scattering technologies.

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