Coherent population trapping in two-electron three-level systems with aligned spins

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Abstract

The possibility of coherent population trapping in two electron states with aligned spins (ortho-system) is evidenced. From the analysis of a three-level atomic system containing two electrons, and driven by the two laser fields needed for coherent population trapping, a conceptually new kind of two-electron dark state appears. The properties of this trapping are studied and are physically interpreted in terms of a dark hole, instead of a dark two-electron state. This technique, among many other applications, offers the possibility of measuring, with subnatural resolution, some superposition-state matrix-elements of the electron-electron correlation that due to their time dependent nature are inaccessible by standard measuring procedures.

42.50.Gy, 32.80.Qk, 31.25.Jf
Coherent manipulation of the atomic wavefunction by laser fields allows the preparation of the atom in particular states with surprising properties due to the constructive or destructive interference of the wavefunction. The presence of non-absorption resonances or dark states is well known since the late seventies [1] [2] [3]. From those initial times the physical properties of the dark and bright states have been fruitfully employed in thousands of different situations [4]. Related concepts such as Electromagnetically Induced Transparency, Amplification Without Inversion, or Lasing Without Inversion, have been also introduced over the last years [5] [6].

Most of the related experiments deal with single electron atoms, or single active electron situations, where an electron is coherently forced to a superposition state. In a two electron system, however, the situation can be a bit different because of the electron-electron interaction and particularly because of the Pauli exclusion principle. If both electrons are not allowed to be at the same state at the same time, the dynamics of one of them will strongly influence the dynamics of the second one. Of course, to evidence this effect one needs to work with electrons having parallel spins. If spins were antiparallel, then both of them could be allowed in the same atomic (spatial) state. There are some studies that use related properties of the two electron systems in case of antiparallel spins [4], in different contexts, namely double-core resonance in two-electron atoms.

In the present letter we restrict ourselves to the case of a two-electron ortho-system [8], i.e. a case in which both electrons have parallel spins and therefore the Pauli exclusion principle acts on the spatial part of the wavefunctions. This prevents both electrons to be in the same spatial state. For the case of coherent population trapping this has rich consequences of a very fundamental nature that have never been considered before. We present the general case, we discuss some possibilities for experimental realization of such a system, and we propose the use of coherent population trapping to measure some time-dependent electron-electron interaction matrix elements.

Let us consider a typical V-configuration of the three single-electron states, as indicated in Fig. 1, labelled $\ket{a}$, $\ket{b}$, and $\ket{c}$, with energies $\hbar \omega_a$, $\hbar \omega_b$, and $\hbar \omega_c$ respectively. If two of
these states are populated, we can build up antisymmetrized two-electron states. Since two electrons with aligned spins are considered, the spin term is symmetric and the antisymmetry of the total wave function comes from the spatial part of the wavefunction.

The three level system is formed by two adjacent dipole transitions sharing a common state $|c\rangle$. The dipole coupling to the laser fields, $H_{\text{dip}}$, is given by $\langle a|H_{\text{dip}}|c\rangle = \hbar \alpha e^{-i\omega_\alpha t}$, and $\langle b|H_{\text{dip}}|c\rangle = \hbar \beta e^{-i\omega_\beta t}$, where $\alpha$ and $\beta$ are the Rabi frequencies of the two laser fields, and $\omega_\alpha$ and $\omega_\beta$ represent their frequencies. We assume that all three single-electron states involved have definite parity, with states $|a\rangle$ and $|b\rangle$ having the same parity and state $|c\rangle$ having the opposite one. Therefore, $\langle a|H_{\text{dip}}|a\rangle = \langle b|H_{\text{dip}}|b\rangle = \langle c|H_{\text{dip}}|c\rangle = 0$, and also $\langle a|H_{\text{dip}}|b\rangle = 0$.

We introduce the Rotating Wave Approximation [2] [9], just keeping slow oscillations at frequencies comparable to the detunings, $\Delta_\alpha = \omega_\alpha - (\omega_a - \omega_c)$, and $\Delta_\beta = \omega_\beta - (\omega_b - \omega_c)$. To describe the long-time dynamics of this system is necessary to consider relaxation. We introduce the relaxation coefficient $\gamma_{ac}$, indicating the rate of decay of the population from state $|a\rangle$ (the uppermost level) to state $|c\rangle$, and the relaxation coefficient $\gamma_{bc}$, indicating the rate of decay of the population from state $|b\rangle$ to state $|c\rangle$. In the dipole approximation, $\gamma_{ba} = \gamma_{ab} = 0$.

Let us consider now that two electrons (in the same spin state) are forced to be inside this three-level system. The two-electron states are indicated by $|i,j\rangle = |i\rangle \otimes |j\rangle$, with $i,j = a,b,c$. Antisymmetrized states are $|A\rangle = \frac{1}{\sqrt{2}} (|c,b\rangle - |b,c\rangle)$, $|B\rangle = \frac{1}{\sqrt{2}} (|a,c\rangle - |c,a\rangle)$, and $|C\rangle = \frac{1}{\sqrt{2}} (|a,b\rangle - |b,a\rangle)$. Without considering electron-electron interaction, the energies of those states are given by $\hbar$ times $\omega_A = \omega_h + \omega_c$, for state $|A\rangle$, $\omega_B = \omega_a + \omega_c$, for state $|B\rangle$, and $\omega_C = \omega_a + \omega_b$, for state $|C\rangle$.

Parity of the two-electron states is directly related to the parity of the single-electron states. Two electron states will thus keep a well defined parity. In particular, $|A\rangle$ and $|B\rangle$ will be of the same parity and $|C\rangle$ of the opposite one. The two-electron states non-vanishing dipole matrix elements will be: $\langle C|H_{\text{dip}}|A\rangle = \hbar \alpha e^{-i\omega_\alpha t}$, and $\langle C|H_{\text{dip}}|B\rangle = \hbar \beta e^{-i\omega_\beta t}$ and all other couplings are zero because of parity considerations, $\langle A|H_{\text{dip}}|A\rangle = \langle B|H_{\text{dip}}|B\rangle = \langle C|H_{\text{dip}}|C\rangle = \langle A|H_{\text{dip}}|B\rangle = 0$. These two-electron states determine now a Λ-configuration,
as indicated in Fig. 2, while the one-electron states $|a\rangle$, $|b\rangle$, $|c\rangle$ formed a V-configuration.

The density matrix for the two-electron three-level system is defined by $(\rho)_{IJ} = |I\rangle\langle J|$, with $I, J = A, B, C$. Still without considering the electron-electron interaction, the dynamical equations for the two-electron density matrix are,

$$
\frac{d}{dt}\rho_{AA} = i[\rho_{AC}\alpha - \rho_{AC}^*\alpha^*] + \gamma_{CA}\rho_{CC}
$$

(1a)

$$
\frac{d}{dt}\rho_{BB} = i[\rho_{BC}\beta - \rho_{BC}^*\beta^*] + \gamma_{CB}\rho_{CC}
$$

(1b)

$$
\frac{d}{dt}\rho_{CC} = i[-\rho_{AC}\alpha + \rho_{AC}^*\alpha^* - \rho_{BC}\beta + \rho_{BC}^*\beta^*] - (\gamma_{CA} + \gamma_{CB})\rho_{CC}
$$

(1c)

$$
\frac{d}{dt}\rho_{AB} = i[-\rho_{AC}(\Delta_\alpha - \Delta_\beta) + \rho_{AC}\beta - \rho_{BC}^*\alpha^*] - \Gamma_{AB}\rho_{AB}
$$

(1d)

$$
\frac{d}{dt}\rho_{AC} = i[-\rho_{AC}\Delta_\alpha + \alpha^*(\rho_{AA} - \rho_{CC}) + \rho_{AB}\beta^*] - \Gamma_{AC}\rho_{AC}
$$

(1e)

$$
\frac{d}{dt}\rho_{BC} = i[-\rho_{BC}\Delta_\beta + \beta^*(\rho_{BB} - \rho_{CC}) + \rho_{AB}^*\alpha^*] - \Gamma_{BC}\rho_{BC}
$$

(1f)

The relaxations correspond to single electron processes, $\gamma_{CA} = \gamma_{ac}$, $\gamma_{CB} = \gamma_{bc}$, indicate an electron falling from state $|a\rangle$ to state $|c\rangle$, and from state $|b\rangle$ to state $|c\rangle$, respectively. Dipole decay between states $|a\rangle$ and $|b\rangle$ is forbidden by parity: $\gamma_{BA} = \gamma_{ab} = 0$, and $\gamma_{AB} = \gamma_{ba} = 0$.

The two-electron coherences will relax according to: $2\Gamma_{BA} = \gamma_{BA} + \gamma_{AB} = 0$, $2\Gamma_{AC} = \gamma_{CA} + \gamma_{CB} = \gamma_{ac} + \gamma_{bc}$, and $2\Gamma_{BC} = \gamma_{CA} + \gamma_{CB} = \gamma_{ac} + \gamma_{bc}$. No simultaneous two-electron relaxation mechanisms will be considered, because they are forbidden in the electric dipole approximation.

Following standard ideas of solid state physics we can interpret that we have two electrons to fill three states, $|a\rangle$, $|b\rangle$, and $|c\rangle$. So there are two occupied states plus an empty one, the hole. The system is thus characterized by the position of the hole. The two-electron state $|C\rangle$, for example, involves one electron at state $|a\rangle$ and the second electron at state $|b\rangle$, leaving the $|c\rangle$ empty.

It is perfectly well established [1] [2] [3], that under certain conditions the two lower states form a very peculiar coherent superposition. The result is that a state $|d\rangle$ uncoupled to the laser fields and another state $|e\rangle$ coupled to the laser fields appear. These single-electron states are not precisely the typical dark and bright states because they correspond to the
two upper states of the V-configuration and relax very fast. In the particular case that the Rabi frequencies of both transitions are equal, $\alpha = \beta$, and the detunings verify $\Delta_\alpha = \Delta_\beta$, then the expressions of the dark, $|d\rangle$, and the bright, $|e\rangle$, states are extremely simple and symmetrical, $|d\rangle = \frac{1}{\sqrt{2}}(|a\rangle - |b\rangle)$, and $|e\rangle = \frac{1}{\sqrt{2}}(|a\rangle + |b\rangle)$.

We can repeat the procedure to obtain the dark states now using two-electron states. The result is that a dark state $|D\rangle$ and a bright state $|E\rangle$ appear. In the particular case of equal Rabi frequencies, $\alpha = \beta$, and equal detunings $\Delta_\alpha = \Delta_\beta$, then the dark state is $|D\rangle = \frac{1}{\sqrt{2}}(|A\rangle - |B\rangle)$ and the bright state is $|E\rangle = \frac{1}{\sqrt{2}}(|A\rangle + |B\rangle)$. Now the dark state $|D\rangle$ involves one electron in a superposition of the upper states $|a\rangle$ and $|b\rangle$, while the other electron lies in the lowest energy state $|c\rangle$. Therefore a hole appears in the empty upper state. Relaxation does not play a role now because the lower state is filled with an electron and Pauli exclusion principle does not allow a second one in the same state. Therefore this dark state has the appearance of a hole that is moving between the two upper single electron states. To illustrate this we have included a new scheme of the single electron states. Fig. 3a correspond to only one electron (grey circle) in the system. Under the appropriated conditions, the electron can be placed in a state $|d\rangle$ that is not coupled to the fields. This state, however, can decay. In the case of two electrons, Fig. 3b, there is one electron at the lower state that prevents the decay from the upper states. The state without electron, the hole, is trapped and stable. Therefore, we have now a hole placed at a dark state!

We have so far considered two-electron systems where the electron-electron interaction is not accounted for. Only the Pauli exclusion principle has been considered through the antisymmetrization of the spatial part of the wave function (spin part is always symmetrical in the considered ortho-atom). The two-electron system can be understood in terms of a hole. Of course this agreement is so far perfect because we have forgotten one particular feature, the electron-electron repulsion. Now it is time to consider these terms and see how they modify the presented results. The interaction Hamiltonian is $H_{ee} = e^2/|r_1 - r_2|$, $r_1$ and $r_2$ being the positions of the electrons, then
\[ \langle A | H_{ee} | A \rangle = \langle cb | H_{ee} | cb \rangle - \langle cb | H_{ee} | bc \rangle = \hbar \Delta_A \quad (2a) \]
\[ \langle B | H_{ee} | B \rangle = \langle ca | H_{ee} | ca \rangle - \langle ca | H_{ee} | ac \rangle = \hbar \Delta_B \quad (2b) \]
\[ \langle C | H_{ee} | C \rangle = \langle ba | H_{ee} | ba \rangle - \langle ba | H_{ee} | ab \rangle = \hbar \Delta_C \quad (2c) \]
\[ \langle A | H_{ee} | C \rangle = \langle cb | H_{ee} | ab \rangle - \langle cb | H_{ee} | ba \rangle = 0 \quad (2d) \]
\[ \langle B | H_{ee} | C \rangle = \langle ca | H_{ee} | ab \rangle - \langle ca | H_{ee} | bc \rangle = 0 \quad (2e) \]
\[ \langle A | H_{ee} | B \rangle = \langle cb | H_{ee} | ac \rangle - \langle cb | H_{ee} | ca \rangle = \hbar \chi e^{-i\omega_b t} e^{i\omega_a t} \quad (2f) \]

These electron-electron interaction terms can be grouped in two different families, the time-independent terms (that do not contain time oscillations at the energy difference) and the time-dependent terms (that do contain explicit time oscillations). Time independent terms come from the diagonal matrix elements \( \langle A | H_{ee} | A \rangle, \langle B | H_{ee} | B \rangle, \langle C | H_{ee} | C \rangle \). The contributions \( \langle c, b | H_{ee} | c, b \rangle, \langle c, a | H_{ee} | c, a \rangle \), and \( \langle b, a | H_{ee} | b, a \rangle \), are Coulomb terms. The contributions \( \langle c, b | H_{ee} | b, c \rangle, \langle c, a | H_{ee} | a, c \rangle \), and \( \langle b, a | H_{ee} | a, b \rangle \), are exchange terms. For a system in a pure quantum state only these two kind of electron-electron terms are relevant. With the dynamical situation established via the interaction with the laser fields, electrons are in superposition states and, thus, new terms may appear that are time dependent. The term, \( \langle A | H_{ee} | B \rangle \) is very particular because it involves three different one-electron states. It is the sum of two different contributions \( \langle c, b | H_{ee} | a, c \rangle \), and \( \langle c, b | H_{ee} | c, a \rangle \). The cross term \( \langle cb | H_{ee} | ac \rangle \) involves the two dipole-allowed transitions, \( |a\rangle \leftrightarrow |c\rangle \) for one electron, and \( |c\rangle \leftrightarrow |b\rangle \) for the other electron. Another cross term that appears is \( \langle c, b | H_{ee} | c, a \rangle \), it is different to the first one because one of the electrons remains in the common state \( c \) while the other is in a \( |a\rangle \leftrightarrow |b\rangle \) coherence. In any case, these two terms present a time oscillation at frequency \( \omega_a - \omega_b \), so the resulting electron-electron matrix element can be written as, \( \langle A | H_{ee} | B \rangle = \hbar \chi e^{-i\omega_b t} e^{i\omega_a t} \).

Finally, let us remember that due to parity considerations, \( \langle A | H_{ee} | C \rangle = \langle B | H_{ee} | C \rangle = 0 \) because \( H_{ee} \) is an even operator.

Now we can introduce the \( H_{ee} \) couplings in the time evolution of the density matrix. To simplify the expressions it is worth to consider as the energy origin the corrected energy of state \( |A\rangle \). After introducing the rotating wave approximation, we obtain a new system of
dynamical equations

\[
\frac{d}{dt}\rho_{AA} = i \left[\rho_{AC}\alpha - \rho_{AC}\alpha^*\right] + \gamma_{CA}\rho_{CC} + i \left[\rho_{AB}^*\chi e^{i\omega_a t}e^{-i\omega_b t} - \rho_{AB}\chi^*e^{-i\omega_a t}e^{i\omega_b t}\right]
\]

\[
\frac{d}{dt}\rho_{BB} = i \left[\rho_{BC}\beta - \rho_{BC}\beta^*\right] + \gamma_{CB}\rho_{CC} + i \left[\rho_{AB}\chi^*e^{-i\omega_a t}e^{i\omega_b t} - \rho_{AB}^*\chi e^{i\omega_a t}e^{-i\omega_b t}\right]
\]

\[
\frac{d}{dt}\rho_{CC} = i \left[-\rho_{AC}\alpha + \rho_{AC}\alpha^* - \rho_{BC}\beta + \rho_{BC}\beta^*\right] - (\gamma_{CA} + \gamma_{CB})\rho_{CC}
\]

\[
\frac{d}{dt}\rho_{AB} = i \left[-\rho_{AC}\Delta_{\alpha} + \rho_{AC}\alpha^* - \rho_{BC}\beta + \rho_{BC}\beta^*\right] - \Gamma_{AB}\rho_{AB} + i \left[\rho_{AA} - \rho_{BB}\right]\chi e^{-i\omega_a t}e^{i\omega_b t} + \rho_{AB}\left(\Delta_A - \Delta_B\right)
\]

\[
\frac{d}{dt}\rho_{AC} = i \left[-\rho_{AC}\Delta_{\alpha} + \rho_{AC}\alpha^* - \rho_{CC}\beta + \rho_{CC}\beta^*\right] - \Gamma_{AC}\rho_{AC} + i \left[\rho_{AC}\Delta_C - \rho_{BC}\chi^*e^{i\omega_a t}e^{i\omega_b t}\right]
\]

\[
\frac{d}{dt}\rho_{BC} = i \left[-\rho_{BC}\Delta_{\beta} + \rho_{CC}\beta - \rho_{AB}\alpha + \rho_{AB}\alpha^*\right] - \Gamma_{BC}\rho_{BC} + i \left[\rho_{BC}\Delta_C - \rho_{AC}\chi e^{i\omega_a t}e^{-i\omega_b t}\right]
\]

One very clear example where coherent population trapping of this kind is calcium, or other alkaline-earth elements. In the ortho-atom case (parallel spins) the ground state is of the form \(n snp\) (4s4p for calcium). One excited state very interesting for our purposes is the \(npnp\). The transition energy is about 2.9 eV for calcium. If a \(\sigma^+\), \(\sigma^-\) laser field is considered, then the three single electron states involved will be \(|a\rangle = |np_+\rangle\), \(|b\rangle = |np_-\rangle\), and \(|c\rangle = |ns\rangle\). Obviously, the three-two electron states will become \(|A\rangle = |ns, np_-\rangle\), \(|B\rangle = |ns, np_+\rangle\), and \(|C\rangle = |np_+, np_-\rangle\). In this particular case, \(\langle A\mid H_{ee}\mid B\rangle = 0\) due to the angular momentum addition laws [10]. Because \(n n_{np_+}\) and \(n n_{np_-}\) correspond to the ground state of the ortho-atom, they are relatively stable. In that case a clear dark state can be formed with all the characteristics of the coherent population trapping, except that the trapping affects the hole, that is in a coherent superposition of the two excited single-electron states. Other similar systems can be found in atoms with more than two electrons in the external shell. This structure is also present in ortho-lithium (lithium with three aligned spins) involving the 1s2s2p and 1s2p2p states.
On the opposite case, for atoms or molecules where the $\langle A|H_{ee}|B\rangle$ matrix element is non-zero, we predict a similar dark resonance but shifted by an amount equal to the time average of the $\langle A|H_{ee}|B\rangle$ coupling. This suggests a new method to calculate electron-electron correlations with subnatural resolution. To illustrate this, Fig. 4 has been included. This figure represents the spectra of the dark state resonance and its two satellites induced by the crossed correlations terms of the electron-electron interaction. It is a plot the imaginary part of the $|A\rangle \leftrightarrow |C\rangle$ coherence versus the $\Delta_\alpha$ detuning, and corresponds to $\gamma_{ac} = \gamma_{bc}$, $\alpha = 0.1\gamma_{bc}$, $\beta = 0.1\gamma_{bc}$, $\Delta_\beta = 0$, and $\chi = 0.3\gamma_{bc}$. For simplicity, all parameters have been given referred to $\gamma_{bc}$.

Coherent population trapping appears at the center $\Delta_\alpha = 0$, as expected. Moreover, two satellite holes appear at $\pm \chi$. They are due to the splitting of the levels induced by the time-dependent matrix element and to its coupling to the laser field. The dressed transitions responsible for those peaks are depicted at the insets of Fig. 4.

In conclusion we have analyzed the dynamical properties of a three-level two-electron system. The presence of a coherence between the atomic two-electron states leads to population trapping similar to the one found in one-electron systems. However, this two-electron trapping presents some new and interesting features. Particularly remarkable is the presence of a hole (the empty state) trapped in a superposition of the upper states. In the case where the two lower states are coupled by the electron-electron potential, we propose a direct subnatural measure of these coupling coefficients.

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FIGURES

FIG. 1. Schematic representation of the single-electron states, $|a\rangle$, $|b\rangle$, and $|c\rangle$, in a V configuration.

FIG. 2. Schematic representation of the two-electron states, $|A\rangle$, $|B\rangle$, and $|C\rangle$, that automatically are arranged in a Λ configuration.

FIG. 3. Representation of three level single-electron system. If only one electron is considered (a) a uncoupled state $|d\rangle$ appears as a superposition of the two excites states. State $|d\rangle$ may decay to the lower state. If two electrons are considered (b) there is a hole that can be trapped in this uncoupled state. This hole can not relax to any other state.

FIG. 4. Spectra of the dark state resonance and its two satellites induced by the crossed correlations terms of the electron-electron interaction. Figure represents the imaginary part of the AC coherence versus the detuning $\Delta/\gamma_{bc}$. It corresponds to $\gamma_{ac} = \gamma_{bc}$, $\alpha = \beta = 0.1\gamma_{bc}$, $\Delta_\beta = 0$, and $\chi = 0.3\gamma_{bc}$. The three insets indicate the dressed-level couplings that contribute to each dark resonance.
REFERENCES

[1] G. Alzetta, A. Gozzini, L. Moi and G. Orriols, Nuovo Cimento B 36, 5 (1976); E. Arimondo and G. Orriols, Lett. Nuovo Cimento 17, 333 (1976); G. Alzetta, L. Moi and G. Orriols, Nuovo Cimento B 52, 205 (1979).

[2] G. Orriols, Nuovo Cimento B 53, 1 (1979).

[3] H. R. Gray, R. M. Whitley and C. R. Stroud, Jr., Opt. Lett. 3, 218 (1978).

[4] For a recent and complete review, see E. Arimondo, in Progress in Optics, edited by E. Wolf, (Elsevier, Amsterdam, 1996), Vol. 35, p. 257.

[5] S. E. Harris, Physics Today, 50 36 (1997)

[6] See, for example, J. Mompart, and R. Corbalán J. Opt. B: Quantum Semiclass. Opt, 2, R7 (2000)

[7] R. Grobe, S. L. Haan, and J. H. Eberly, Phys. Rev A 54, 1516 (1996)

[8] For analogy with the standard terminology with helium (ortho-helium for the atom with parallel spins -triplet- and para-helium for the atom with antiparallel spins -singlet-) we will refer throughout the paper to ortho-atom and para-atom, and to ortho-system and para-system.

[9] See, for example, Robert W Boyd, Nonlinear Optics, Academic Press, 1992.

[10] See, for example, A R Edmons, Angular Momentum in Quantum Mechanics, Princeton Univ. Press, 1974.
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