Chapter 2
Quantum Switching of Magnetic Fields by Circularly Polarized Re-Optimized $\pi$ Laser Pulses: From One-Electron Atomic Ions to Molecules

Ingo Barth and Jörn Manz

Abstract Circularly polarized re-optimized $\pi$ laser pulses may induce electronic and/or nuclear ring currents in model systems, from one-electron atomic ions till molecules which should have three-, four-, or higher-fold axes of rotations or reflection-rotations, in order to support doubly or more degenerate, complex-valued eigenstates which support these ring currents. The ring currents in turn induce magnetic fields. The effects are about two orders of magnitude larger than for traditional ring currents which are induced by external magnetic fields. Moreover, the laser pulses allow to control the strengths and shapes of the ring currents and, therefore, also the induced magnetic fields. We present a survey of the development of the field, together with new quantum simulations which document ultrafast switchings of magnetic fields. We discuss various criteria such as strong ring currents with small radii, in order to generate huge magnetic fields, approaching 1.000 T, in accord with the Biot–Savart law. Moreover, we consider various methods for monitoring the fields, and for applications, in particular ultrafast deflections of neutrons by means of quantum switching of the ring currents and induced magnetic fields.

I. Barth (✉)
Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany
and
Kavli Institute for Theoretical Physics, University of California, Santa Barbara, California 93106–4030, USA
and
Max-Born-Institut, Max-Born-Str. 2A, 12489 Berlin, Germany
e-mail: barth@mbi-berlin.de

J. Manz
Institut für Chemie und Biochemie, Freie Universität Berlin, Takustr. 3, 14195 Berlin, Germany
and
Kavli Institute for Theoretical Physics, University of California, Santa Barbara, California 93106–4030, USA
e-mail: jmanz@chemie.fu-berlin.de

K. Yamanouchi, G. Gerber and A. D. Bandrauk (eds.),
Progress in Ultrafast Intense Laser Science VI,
Springer Series in Chemical Physics 99, DOI 10.1007/978-3-642-15054-8_2,
© Springer-Verlag Berlin Heidelberg 2010
2.1 Introduction

Recent quantum dynamics simulations predict that circularly polarized laser pulses may induce stationary ring currents or time-dependent charge circulations in model systems, with applications from the hydrogen atom or one-electron atomic ions [1, 2] to molecules [3–13], see also [14, 15], circular carbon clusters [16], nanorings [17–20], and nanotubes [21]; for pioneering applications to Rydberg states see [22–27]. These ring currents and charge circulations in turn induce stationary [2, 4, 7–9, 28] and time-dependent [28] magnetic fields in the model systems, respectively. From a theoretical perspective, a stationary ring current is described in terms of a single complex stationary degenerate eigenfunction of the system, carrying angular momentum; different eigenstates correspond to different ring currents and, therefore, to different induced stationary magnetic fields [28]. As a rule, the corresponding stationary densities and charge distributions often have typical toroidal or near-toroidal shapes [2, 7–9, 11, 28]; exceptions from this rule (e.g., for ring-shaped molecules) are documented in [4, 28], see also Fig. 2.3b below. Recently, this characteristic signature has been observed experimentally in ionized states of atoms induced by well-designed circularly polarized laser pulses [29]. In contrast, charge circulations, i.e., non-stationary ring currents, are represented by time-dependent wave packets, which carry non-zero angular momentum, and corresponding time- and angle-dependent densities; again as a rule, the centers of these non-stationary densities and corresponding charge distributions move along toroidal or near-toroidal paths about the axis of symmetry (e.g., molecular axis) [10, 12, 28]; for exceptions from this rule (e.g., for ring-shaped molecules) see [3, 5, 6, 28]. These wave packets are also called “hybrid states” which are superpositions of at least one of the complex eigenfunctions which support ring currents, plus others which have different eigenenergies, e.g., the ground state.

The condition that laser-induced ring currents supporting magnetic fields are represented by complex eigenfunctions is essential because otherwise real eigenfunctions (or eigenfunctions which are real except for a phase factor) would yield zero flux/current densities, see e.g., [28, 30–32]. At the same time, this condition imposes the constraint of special symmetries for suitable model systems, i.e., they should support at least one, two- or higher-dimensional irreducible representation with corresponding doubly or more degenerate symmetry-adapted basis functions. This requirement is satisfied automatically for model systems which possess a principle axis of $n$-fold rotation or rotation–reflection, where $n \geq 3$, including the H atom and one-electron atomic ions ($n = \infty$) [1, 2], or linear molecules ($n = \infty$) [7–12] and nanorings ($n \approx \infty$) [17–20], or molecules which have, e.g., $D_{nh}$ symmetry ($n \geq 3$) such as Mg-porphyrin ($n = 4$) [3–6] or benzene ($n = 6$); other possible symmetries include $C_{nv}$ ($n \geq 3$), $D_{nd}$ ($n \geq 2$), or tetrahedral (e.g., CH$_4$, UH$_4$, or more generally AB$_4$) or icosahedral molecules (e.g., C$_{60}$) or clusters, If the ideal symmetry of the system is just “weakly broken” such that it possesses near-degenerate states, it may still support temporary charge circulations [33, 34]. All other molecules do not allow excitations of ring currents (e.g., there are no stationary ring currents in molecules with $D_{2h}$ symmetry such as ethylene, because
circularly polarized laser pulse

ring current
(electronic or nuclear)

induced magnetic field

Fig. 2.1 Induction of ring currents and magnetic fields by circularly polarized laser pulses (schematic)

$D_{2h}$ has only one-dimensional irreducible representations. Below we shall focus on quantum switching of magnetic fields which are supported by ring currents in systems with suitable symmetries. The term “quantum” implies quantum dynamics simulations of the processes which are induced by means of well-designed laser pulses. “Switching” is understood in the general sense, i.e., switching-on and -off, or switching the direction of the magnetic fields. These effects will be achieved simply by switching-on and -off the underlying ring currents, or switching their directions, e.g., from “left” to “right” ring currents (for a discussion of the definitions of left versus right circularly polarized fields and corresponding ring currents, see [4] and the literature cited therein).

The net effect from circularly polarized laser pulses via ring currents to induced magnetic fields in model systems with proper symmetry is sketched schematically in Fig. 2.1. It is related to the Inverse Faraday Effect [35–37]. The photons of the left and right circularly polarized laser pulses carry angular momenta $\hbar$ with opposite helicities, which are transferred to the system causing corresponding opposite changes of the angular momenta of the ring currents, e.g., from the non-degenerate ground state to degenerate excited states with opposite magnetic quantum numbers $-\hbar$ or $+\hbar$, respectively. Since the circularly polarized driving fields $E(t)$ may be decomposed into two perpendicular components (say $E_X(t)$ and $E_Y(t)$) perpendicular to the direction of propagation (say $Z$, in the laboratory frame), similar effects may also be achieved by more general laser pulses which possess two perpendicular components with proper phase relationships, [12, 17, 33, 34], e.g., optimal control fields [20]. Experimental preparations of these types of circularly polarized or more general laser pulses have been demonstrated, e.g., in [38–42], see also [43].

The ring currents and magnetic fields induced by laser pulses turn out to be much stronger (typically by two orders of magnitude) than those induced by the traditional approach which is based on applying static external magnetic fields, compare, e.g., [4] and [44, 45] (see also the reviews [46–48]), respectively. The reason is that laser pulses can induce currents which correspond to excitations of full charges (e.g., $-1e$ for single electron excitation), or even more. In contrast, present technology restricts the strength of permanent external magnetic fields to less than 100 T [49], and these
magnetic fields may induce only rather weak ring currents corresponding to stationary fluxes of $-1/100$ e or less. Indeed, one would need external permanent magnetic fields of the order of $10,000\,\text{T}$ in order to induce similarly strong effects as laser pulses – a scenario which exists in cosmic domains, see e.g., [50–52], but which is far out of reach of present technology in the laboratory. This comparison indicates the enormous advantage of the suggested new approach to ring currents and induced magnetic fields, generated by circularly polarized laser pulses.

Another fundamental advantage is that laser pulses allow active control of the strengths and shapes of the ring currents and, therefore, also the magnetic fields, simply by exciting different degenerate eigenstates, by means of well-designed control laser pulses [28]. In contrast, from a theoretical perspective, permanent external magnetic fields even as strong as $100\,\text{T}$ are still in the weak-field that is linear response regime, i.e., they do not allow any control of the induced ring currents. The second advantage, i.e., controllability, puts the present topic into the general realm of quantum control by means of laser pulses, see e.g., [53–55].

The purpose of this article is twofold: In Sect. 2.2, we present a survey of the development of the field, focusing on our approach which is based on circularly polarized re-optimized $\pi$ laser pulses applied to model systems from the hydrogen atom or one-electron atomic ions and to pre-oriented/aligned molecules, in the non-relativistic regime [2, 4, 7–9, 11, 28]; for relativistic extensions including ring currents caused by electron spins, see e.g., [56], see also [57]. Quantum control by $\pi$ laser pulses, or series of $\pi$ laser pulses, is based on some experience of our group which goes back to state-selective bond breaking [58], and subsequent extensions including control of isomerization reactions by pump-dump IR $\pi$ pulses [59, 60], photo-association [61], as well as separation of enantiomers [62–64]; see also [65–68] and the reviews [69–71]. Section 2.2 will also present the nomenclature and discuss the necessary conditions for observing the effects. Most of these applications deal with switching-on the ring currents and corresponding magnetic fields starting from the systems in the non-degenerate ground state. Reversibility of time and helicity implies that subsequent application of the dump laser pulse would induce the opposite effect, i.e., switching-off; in practice, deviations from perfect reversibility might cause competition of other processes, e.g., climbing to higher levels. In Sect. 2.3, we shall present an extension, i.e., we shall assume that the system has already been switched on to a complex eigenstate, which represents a ring current with corresponding magnetic field, and then we shall show how one can employ a sequential series of re-optimized $\pi$ laser pulses with opposite circular polarizations in order to switch the original direction of the ring currents to the opposite one, together with the associated switch of the direction of the magnetic fields. The concept is motivated by pioneering work by E.K.U. Gross and coworkers who could demonstrate the switch of the directionality of the ring currents in nanorings, by means of optimal laser pulses with a change of the helicity [20]. The conclusions are in Sect. 2.4, including an outlook to applications to favorable systems, and to analysis and control of nuclear vibrations and chemical reactions induced by ultrafast interactions with neutrons, due to pulsed deflections by switched magnetic fields.
2.2 Survey on Quantum Switching-on the Ring Currents and Magnetic Fields

Our previous work on quantum switching-on the ring currents and magnetic fields by means of circularly polarized re-optimized $\pi$ laser pulses has been developed as documented in full detail in [2, 4, 7–9, 11, 28]. The present survey aims at a presentation of the essentials. For this purpose, let us start with setting the exemplary scenario, i.e., we assume that the system is excited by means of a right (+) or left (−) circularly polarized re-optimized $\pi$ laser pulse which propagates along the $Z$-axis in the laboratory frame, with electric field centered at the time $t = 0$

$$E_\pm(t) = E_0 s(t) \left( \cos(\omega t + \eta) e_X \pm \sin(\omega t + \eta) e_Y \right),$$

(2.1)

where $E_0$ is the amplitude, $\omega$ the carrier frequency, $\eta$ the phase, and $e_X$ and $e_Y$ the unit vectors point along the $X$- and $Y$-directions. The electric field may also be defined in terms of the vector field,

$$E_\pm(t) = -\frac{d}{dt} A_\pm(t),$$

(2.2)

see e.g., [6–11, 28]. This option is recommended in particular for ultrashort, few-cycle laser pulses because the resulting electric fields satisfy automatically the condition [72],

$$\int_{-\infty}^{\infty} E_\pm(t) \, dt = 0.$$

(2.3)

The phase $\eta$ turns out to be irrelevant for the present applications to excitations of stationary ring currents and will be set to zero; in contrast, the phase may be significant in the case of excitations of time-dependent charge circulations, see e.g., [73] and Sect. 2.1, and for switching, see Sect. 2.3. The shape functions $s(t)$ of transform-limited experimental laser pulses are Gaussian envelopes, which are well approximated by $\cos^n$ laser envelopes, in the limit $n \to \infty$ [74]; see also [6]. The application for Mg-porphyrin shown below employ a $\cos^2$ laser pulse, the others use, however, the traditional $\cos^2$ shape function, as suggested in [65],

$$s(t) = \begin{cases} 
\cos^2(\pi t / t_p) & \text{for } |t| \leq t_p / 2 \\
0 & \text{for } |t| > t_p / 2 
\end{cases},$$

(2.4)

where $t_p$ denotes the total pulse duration. The full width at half-maximum for the corresponding time-dependent intensity [75]

$$I(t) = c E_0 |E_\pm(t)|^2$$

(2.5)
\[ \tau \approx 0.364 t_p \approx 3.295 \hbar / \Gamma. \] 

(2.6)

where \( \Gamma \) is the spectral width of the laser pulse. The corresponding maximum intensity is

\[ I_{\max} = c \varepsilon_0 c_0^2. \] 

(2.7)

Furthermore, we assume that the system (with system-adapted coordinates \( x, y, z \)) has been suitably pre-oriented or -aligned along the \( Z \)-axis, i.e., \( z = Z \). For atoms or atomic ions, the pre-orientation or -alignment is, of course, unnecessary. Else one may employ any of the techniques which have been developed for orientations or alignments of molecules, see e.g., [76–78]. An explicit example of quantum dynamics simulations for pre-orientation of polar molecules based on the method of [79,80], followed by the excitation of ring currents and magnetic fields, is given in [8,9,28]. In this scenario, initial pre-orientation or -alignment is restricted to a finite period \( \tau_{\text{ori}} \) or \( \tau_{\text{ali}} \), respectively; subsequently, periodic events of similar pre-orientation or -alignment may occur due to rotational revivals. It is mandatory that the ring currents and induced magnetic fields are switched on or off during these periods of pre-orientation or -alignment, i.e., the duration \( \tau \) of the exciting or de-exciting laser pulses must be shorter than \( \tau_{\text{ori}} \) or \( \tau_{\text{ali}} \),

\[ \tau < \tau_{\text{ori}} \quad \text{or} \quad \tau < \tau_{\text{ali}}. \] 

(2.8)

Next let \( H_{\text{sys}} \) be the Hamiltonian of the pre-oriented or -aligned system, with corresponding discrete (bound state) eigenfunctions \( |\psi_i\rangle \) (short-hand notation: \( |i\rangle = |\psi_i\rangle \)) and eigenenergies \( E_i \) which are obtained as solutions of the time-independent Schrödinger equation

\[ H_{\text{sys}} |i\rangle = E_i |i\rangle. \] 

(2.9)

In case of the H atom or one-electron atomic ions, the \( |i\rangle \) are simply the corresponding atomic orbitals (AOs); else one has to employ quantum chemical or other numerical methods in order to determine the eigenstates of the system, see e.g., [7–11]. In semi-classical dipole approximation, the laser driven dynamics is described in terms of the wave packet \( |\psi(t)\rangle \) which is obtained as solution of the time-dependent Schrödinger equation

\[ i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = (H_{\text{sys}} - M \cdot E_{\pm}(t))|\psi(t)\rangle \] 

(2.10)

with dipole operator \( M \). Below, we assume that the laser pulses are not all too strong so that we may neglect competing transitions into the continuum such as bond breaking or ionization. The wave packet \( |\psi(t)\rangle \) may then be expanded in terms of the
eigenstates,

\[ |\Psi(t)\rangle = \sum_i C_i(t)|i\rangle \exp(-iE_i t/\hbar) \tag{2.11} \]

with populations

\[ P_i(t) = |C_i(t)|^2. \tag{2.12} \]

Inserting this ansatz into the time-dependent Schrödinger equation (2.10) yields the equivalent set of differential equations for the time-dependent coefficients

\[ i\hbar \frac{d}{dt} C_j(t) = -\sum_i C_i(t)\langle j|M|i\rangle \cdot E_{\pm}(t) \exp(-i\omega_{ij} t) \tag{2.13} \]

with transition frequencies

\[ \omega_{ij} = \frac{E_i - E_j}{\hbar}. \tag{2.14} \]

In the applications of [2–11, 28], the system is initially in the non-degenerate ground state \( |g\rangle = |0\rangle \), that is, \( C_i(t = t_0 = -t_p/2) = \delta_{0i} \), and the laser frequency \( \omega \) is tuned resonant or near-resonant to a particular transition frequency, specifically for excitation from the ground \( |g\rangle \) to a pair of degenerate excited states, \( |i\rangle = |e_+\rangle \) and \( |i + 1\rangle = |e_-\rangle \), denoted for simplicity as

\[ \tilde{\omega} = \omega_{e+,g} = \omega_{e-,g} = \frac{E_{e_+} - E_g}{\hbar}. \tag{2.15} \]

Here, the complex eigenstates, \( |e_+\rangle \) and \( |e_-\rangle \), may be expressed in terms of two real ones

\[ |e_{\pm}\rangle = \frac{1}{\sqrt{2}}(|e_x\rangle \pm i|e_y\rangle), \tag{2.16} \]

similar to the relations of complex atomic orbitals \( |2p_+\rangle \) and \( |2p_-\rangle \) and real ones \( |2p_x\rangle \) and \( |2p_y\rangle \). Other examples of pairs of degenerate complex eigenstates expressed in terms of two real ones are listed schematically in Fig. 2.2. These examples include such different systems as toroidal electronic states \( |\Pi_+\rangle \) and \( |\Pi_-\rangle \) of linear molecules [81], or excited electronic states \( |E_+\rangle \) and \( |E_-\rangle \), with irreducible representation \( E \), of Mg-porphyrin [4], or pseudorotational states with short-hand notation \( |v_{b,x}^1\rangle = |1^1\rangle \equiv |v_{b,+}\rangle \) and \( |1^{-1}\rangle \equiv |v_{b,-}\rangle \) representing complex linear combinations of the first excited \( x \)- and \( y \)-polarized bending vibrational states \( |v_{b,x}\rangle \) and \( |v_{b,y}\rangle \) of linear triatomic molecules or ions, such as CdH\_2 [10] and FHF\^- [11]. In general, laser pulses may generate superpositions (2.11) of these states plus other ones. Then, we are interested, e.g., in the generation of mean angular momentum or
Fig. 2.2 Complex degenerate eigenstates constructed from degenerate real ones (schematic), see also [28]: (a) atomic orbitals $|p\rangle$ [2]; (b) excited electronic states $|\Pi\rangle$ of linear molecules [7–9]; (c) excited electronic states $|E\rangle$ of Mg-porphyrin with irreducible representations $E$ [3–6]; (d) first excited pseudorotational states of symmetric ($D_{\infty \text{h}}$) triatomic linear molecules, represented in terms of orthogonal degenerate bending states [10,11]

magnetic quantum numbers

$$\langle l(t) \rangle = \sum_{n,l,m} l P_{nlm}(t)$$ \hfill (2.17)
$$\langle m(t) \rangle = \sum_{n,l,m} m P_{nlm}(t)$$ \hfill (2.18)

of superpositions of atomic orbitals, or in the time evolution of the mean values of the bending ($v_b$) or pseudorotational ($l$) quantum numbers

$$\langle v_b(t) \rangle = \sum_{v_b,l} v_b P_{v_b,l}(t)$$ \hfill (2.19)
$$\langle l(t) \rangle = \sum_{v_b,l} l P_{v_b,l}(t)$$ \hfill (2.20)

of superpositions of states $|v_b,l\rangle$.

The pulse duration $\tau$ is chosen such that on one hand, the corresponding spectral width $\Gamma$ is smaller than the energy gap $\Delta E$ between the target and neighboring states with the same irreducible representation,

$$\tau \geq 3.295 \hbar / \Delta E.$$

\hfill (2.21)
cf. (2.6). On the other hand, \( \tau \) should be shorter than the time of pre-orientation or -alignment \( \tau_{\text{ori}} \) or \( \tau_{\text{ali}} \) (if this is required), cf. (2.8), as well as the lifetime \( \tau_e \) of the excited states, which may be limited by spontaneous emission [2] and/or dissipative or other competing processes,

\[
\tau \leq \tau_e. \tag{2.22}
\]

The antagonistic conditions (2.21) and (2.8), (2.22) may restrict the possible choices of \( \tau \) to rather narrow domains of suitable pulse duration, see the discussion in [2]. The general solution (2.11) then reduces to approximately three dominant contributions including the ground and two degenerate excited states of the target level

\[
|\Psi(t)\rangle = C_g(t)|g\rangle \exp(-iE_g t/\hbar) + C_{e_+}(t)|e_+\rangle \exp(-iE_{e_+} t/\hbar) + C_{e_-}(t)|e_-\rangle \exp(-iE_{e_-} t/\hbar). \tag{2.23}
\]

In rotating wave approximation (RWA, cf. [82–85]), the solutions for a right circularly polarized resonant laser pulse are

\[
C_g(t) = \cos \left( \frac{M E_0}{\hbar} \int_{t_0}^{t} s(t') \, dt' \right) \tag{2.24}
\]

\[
C_{e_+}(t) = i \sin \left( \frac{M E_0}{\hbar} \int_{t_0}^{t} s(t') \, dt' \right) \exp(-i\omega t_0) \tag{2.25}
\]

\[
C_{e_-}(t) = 0. \tag{2.26}
\]

where \( M \) denotes the transition dipole matrix element (assuming \( x = X \))

\[
M = \frac{\langle g | M_x | e_x \rangle}{\sqrt{2}}, \tag{2.27}
\]

that is, the right circularly polarized laser pulse transfers population selectively from the ground state \( |g\rangle \), which is assumed to be totally symmetric, to the excited state \( |e_+\rangle \) excluding the decoupled state \( |e_-\rangle \). Inserting the shape function (2.4) then yields complete population transfer, \( C_g(t = t_f = t_p/2) = 0 \) at the final time \( t = t_f \), if

\[
|M E_0 t_p| = \pi \hbar. \tag{2.28}
\]

For the chosen target transition \( |g\rangle \rightarrow |e_+\rangle \) and pulse duration \( \tau \) (cf. (2.8), (2.21), (2.22)), expressions (2.1) and (2.4) together with the condition (2.28) may be considered as definition of a right circularly polarized \( \pi \) laser pulse. The resulting field strength \( E_0 \) should be sufficiently low such that the maximum intensity \( I_{\text{max}} \) (2.7) does not exceed certain thresholds \( I_{\text{thr}} \) for competing processes, e.g., ionization; typical values for one-electron atomic ions and molecules are \( I_{\text{thr}} \approx 10^{15} \text{ W cm}^{-2} \) and \( I_{\text{thr}} \approx 10^{12} \text{ W cm}^{-2} \), respectively. It implies the condition
\[
\tau \geq \frac{0.364 \pi \hbar}{|M| \sqrt{I_{th}/(c e_0)}}, \tag{2.29}
\]
in addition to the inequalities (2.8), (2.21), (2.22). Equivalent expressions are obtained for the corresponding left circularly polarized \(\pi\) laser pulse yielding selective population transfer from the ground \(|g\rangle\) to excited \(|e_{-}\rangle\) states.

The laser parameters for the \(\pi\) pulse (2.8), (2.15), (2.21), (2.22), (2.27), (2.28), and (2.29) serve as reference. Subsequently, these parameters are varied systematically (analogous to [69, 70]) such that the time-dependent Schrödinger equation (2.10) yields optimal populations of the target state \(|e_{+}\rangle\) (or \(|e_{-}\rangle\)) when it is solved numerically, using Runge–Kutta propagation with a large, converged (\(\gg 3\)) set of basis functions in the expansion (2.11). In practice, “optimal populations” of the target state are hardly ever perfectly equal to 1, but usually they are sufficiently close to 1. Accordingly, the corresponding ring currents and magnetic fields which are associated with the target states \(|e_{+}\rangle\) or \(|e_{-}\rangle\) are switched on more or less perfectly. The resulting laser pulses are called re-optimized \(\pi\) laser pulses. The subsequent dump laser pulses with same circular polarizations achieve the corresponding more or less perfect switching-off.

After the preparation of the target electronic eigenstates \(|e_{+}\rangle\) or \(|e_{-}\rangle\), for example, the corresponding three-dimensional (3D) one-electron ring current densities are calculated using

\[
j_{\pm}(R = r_1) = \frac{i \hbar}{2m_e} N \int \cdots \int (\psi_{e_\pm} \nabla \psi_{e_\pm}^* - \psi_{e_\pm}^* \nabla \psi_{e_\pm}) \, d\sigma_1 dq_2 \ldots dq_N \tag{2.30}
\]
with electronic coordinates \(q = (r, \sigma)\) for positions and spins of \(N\) electrons. Various approximations which facilitate the calculations have been developed in [4, 7–9, 28] for electronic ring currents. For example, if the underlying electronic eigenstate \(|e_{\pm}\rangle\) is expressed as multi-configurational wave function which has a single dominant Slater determinant corresponding to single electron excitation, then the multidimensional integral for the current density (2.30) can be reduced to the corresponding 3D current density for the molecular orbital (MO) which carries the electron before or after excitation. If this MO is well approximated as linear combination of atomic orbitals (LCAO-MO), then the current density (2.30) may be decomposed into contributions of the AOs. For analysis of the current densities of the AOs, one may employ analytical expressions which have been derived in [2, 28]; for applications, see [7–9, 28]. Analogous definitions apply to nuclear ring currents [28], with approximation by analytical expressions which have been developed using simple models based on two-dimensional harmonic oscillator wave functions [10, 11, 28].

Integration of the current density \(j_{\pm}(R)\) over a half plane \(S\) yields the electric ring current

\[
I_{\pm} = q \int \int j_{\pm}(R) \cdot dS, \tag{2.31}
\]
which has units of charge per time, where $q$ is the charge of the ring current, e.g., $q = -e$ in the case of ring currents which are stimulated by means of single electron excitation. The corresponding period $\tau_I$ or frequency $\omega_I$ of the current can be calculated using

$$|I_{\pm}| = |q| = \frac{|q| \omega_I}{2\pi}.$$ (2.32)

Moreover, $j_{\pm}(\mathbf{R})$ defines the mean reciprocal radius with respect to the axis of the ring current,

$$\langle R^{-1} \rangle_j = \frac{q \int \int R^{-1} j_{\pm}(\mathbf{R}) \cdot d\mathbf{S}}{I_{\pm}},$$ (2.33)

or the corresponding mean ring current radius of the (unidirectional) ring current [2,28],

$$R_{-1} = \frac{1}{\langle R^{-1} \rangle_j}.$$ (2.34)

The definition (2.34) in terms of the reciprocal value of $R$ (indicated by the subscript $-1$) weighted by the current density is more appropriate than the mean value of $R$, i.e., $R$ weighted by the density, for two reasons: First, the latter would yield paradoxical finite values of a hypothetical “mean ring current radius” even if the mean ring currents are zero. Second, we are interested in the reciprocal mean value of $R$, weighted by the current because we aim at calculations of the induced magnetic field $B_{\pm}(\mathbf{R})$. For a classical ring loop model of a ring current $I_{\pm}$ about the $Z$-axis with radius $R$, the Biot–Savart law yields the value

$$B_{\pm} = \pm \frac{\mu_0 I_{\pm}}{2R} \mathbf{e}_Z$$ (2.35)

at the center of the ring loop, i.e., what matters is the reciprocal value of $R$. Accordingly, estimates of $B_{\pm}$ should employ (2.35) with mean value $R = R_{-1}$ (2.34). More rigorously and also more generally, we use the corresponding quantum mechanical expression

$$B_{\pm}(\mathbf{R}) = -\frac{\mu_0}{4\pi} \int \int \int \frac{j_{\pm}(\mathbf{R}') \times (\mathbf{R} - \mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|^3} dV',$$ (2.36)

in accord with the Biot–Savart law. In the case of nuclear ring currents of pseudorotating molecules, the total ring current can be decomposed into partial ring currents of the individual nuclei, with corresponding charges, radii, and induced magnetic fields [28]. Simple analytical expressions have been derived for locations with special symmetry, e.g., at the center or along the symmetry axis (e.g., $Z$-axis) of the ring current [2,7–9,28].
The classical approximation (2.35) to the Biot–Savart law (2.36) suggests that the induced magnetic field should increase with increasing electric ring currents \( I \), i.e., with increasing charge and frequency of the flux (2.32), and also with decreasing mean ring current radius (2.34). It allows to predict several trends which may be used as working hypotheses for the selection of systems and scenarios with large magnetic fields induced by ring currents. For this purpose, let us consider a simple picture of electronic states with corresponding dominant Slater determinants for electrons in occupied orbitals. In the case of one-electron atomic ions, it suffices to consider directly the corresponding atomic orbitals. Two degenerate complex orbitals (see Fig. 2.2) contribute to ring currents and induced magnetic fields if they are occupied by different numbers of electrons \( n_{\pm} \), i.e., \( (n_{-}, n_{+}) = (0, 1), (1, 0), (0, 2), (2, 0), (1, 2), \) or \( (2, 1) \). For a given irreducible representation, the sizes of the orbitals increase with orbital energy, implying, in general, increasing radii of the ring currents. As a consequence, single electron transitions from occupied non-degenerate orbitals to the lowest unoccupied degenerate orbitals or neighboring ones should induce stronger magnetic fields than transitions to higher degenerate unoccupied orbitals. Likewise, single electron transitions from the lowest quadruply occupied degenerate orbitals to non-degenerate unoccupied orbitals should induce stronger magnetic fields than transitions starting from higher degenerate orbitals with the same irreducible representations. As a special case of these rules, in atomic one-electron ions, the strongest magnetic fields are induced by transitions from \( |1s\rangle \) to \( |2p_{\pm}\rangle \) orbitals [2]. For comparison, the induced magnetic fields in Rydberg states are negligible [22–27].

Another general trend suggested by (2.36), (2.35) is that the induced magnetic fields should increase with decreasing size of the system. This rule is confirmed by the present examples, i.e., the values of \( B_{\pm} \) induced by electronic ring currents increase from rather large polyatomic molecules such as Mg-porphyrin [4, 28] via diatomic molecules [7–9, 28] to one-electron atomic ions [2, 28]. Note, however, that actually \( R \) or \( R_{-1} \) in (2.35), (2.34) refer to the mean radius of the ring current, not to the size of the system, hence one may observe rather large induced magnetic fields even in large molecules, provided they support ring currents with small radii. As an example, the present linear molecule or molecular ion \( \text{CdH}_{2} \) and \( \text{FHF}^{-} \) may be excited in degenerate states \( |v_{b, +}\rangle \) or \( |v_{b, -}\rangle \), cf. Fig. 2.2. These states represent pseudorotations of the nuclei about the molecular axis, corresponding, e.g., to toroidal hydrogen bond in \( \text{FHF}^{-} \) [11] and to ring currents with much smaller radii than the system sizes, e.g., \( R_{-1} = 0.0030 \ \text{a}_{0} \) for the Cd nucleus in pseudorotating \( \text{CdH}_{2} \) – it gives rise to the huge induced magnetic field of 318 T at the center of the Cd nuclear ring current. This value is also supported by the rather large current \( I_{\pm} \) (cf. (2.31), (2.32), (2.35)), which can be estimated by the charge of the nucleus, \( Z_{\text{Cd}} = 48 \), which is hardly shielded by electrons, within the radius of the ring current, and the current frequency which corresponds to the bending frequency, \( \omega I/(2\pi c) = \omega b/(2\pi c) = 629.2 \ \text{cm}^{-1} \) or \( \tau_{I} = 53.0 \ \text{fs} \), thus \( I = 0.91 \ \text{e} \ \text{fs}^{-1} \).

The general results are demonstrated in Figs. 2.3–2.5 for four examples, i.e., electronic or nuclear current densities and induced magnetic fields in excited degenerate states \( |2p_{+}\rangle \) of \( \text{He}^{+} \) [2, 28], \( |5\ 1E_{u+}\rangle \) of Mg-porphyrin [28] as well as the
Fig. 2.3  Electronic ring current densities and induced magnetic fields for excited states (a) |2p_e⟩ of the He^+ ion and (b) |5^1E_u+⟩ of Mg-porphyrin, illustrated by color-coded cuts for the X/Y plane (left panels) and for the Y/Z plane (right panels). The maximum absolute values of the magnetic fields are max |B_{2p_e}(R)| = 4.17 T and max |B_{5^1E_u+}(R)| = 0.11 T. The arrows indicate the directions (adapted from [28])
Fig. 2.4  (a) Nuclear ring current density (illustrated by a gray-scaled cut for the $Y/Z$ plane) and (b) $Z$-component of the induced magnetic field along the molecular $Z$-axis, for the excited pseudorotational state $|1^1\rangle$ of CdH$_2$. The current density close to the central Cd nucleus is zoomed in by a factor 20. The current densities and the magnetic fields close to the polar protons have been amplified by factors 2,000 and 500, respectively (adapted from [28]).

Fig. 2.5  (a) Nuclear ring current density (illustrated by a gray-scaled cut for the $Y/Z$ plane) and (b) $Z$-component of the induced magnetic field along the molecular $Z$-axis, for the excited pseudorotational state $|1^1\rangle$ of FHF$^-$. The current densities close to the polar F nuclei are zoomed in by a factor 5. The current density and the magnetic fields close to the central proton have been amplified by factors 40 and 10, respectively (adapted from [28]).

pseudorotational states $|v_{b, +}\rangle = |1^1\rangle$ of CdH$_2$ [10, 28] and FHF$^-$ [11, 28], respectively. Most of the time, the ring currents turn out to be toroidal and so are also the induced magnetic fields. As an exception, the case of state $|5^1E_{u+}\rangle$ of Mg-porphyrin shows rich structures of ring currents and the induced magnetic field, suggesting forward and backward currents in different domains, according to the molecular topology which connects four sub-rings to one global ring.

Moreover, Figs. 2.6 and 2.7 show the components of the electric fields $E_X(t)$ and $E_Y(t)$, and intensities $I(t)$ of the circularly polarized laser pulses which excite these electronic ring currents, exemplarily for He$^+$ and Mg-porphyrin (panels a), together with the population dynamics (panels b). The results for He$^+$ employ the
Fig. 2.6 (a) $X$- (black solid) and $Y$- (gray solid) components and intensity (dashed) of the circularly polarized $\pi$ laser pulse and (b) the resulting population dynamics of the ground $|1s\rangle$ and excited $|2p_+\rangle$ states of the He$^+$ ion, indicating perfect population transfer from $|1s\rangle$ to $|2p_+\rangle$.

RWA approximation (2.24)–(2.26), whereas the results for Mg-porphyrin have been obtained by numerical solution of the time-dependent Schrödinger equation, using (2.2) with $\cos^{20}$ envelope [28]. Note the huge difference of the laser parameters, from ultrashort, intense laser pulses which are applicable for He$^+$ compared to much longer and less intense laser pulses for Mg-porphyrin. The different durations of the pulses are in accord with conditions (2.8), (2.21), (2.22), (2.29), calling for the different intensities due to (2.5), (2.28) [2,28]. In contrast, these antagonistic conditions do not allow us to design circularly polarized re-optimized $\pi$ pulse for excitations of the nuclear ring currents in CdH$_2$. Nevertheless, excitations of nuclear circulations have been documented in [10,28]. Also note the huge differences of the maximum values of the induced magnetic fields, from 0.1 to 0.2 T in Mg-porphyrin to 318 T at the center of the nuclear ring current of the Cd nucleus in CdH$_2$ – the latter exceeds even the largest permanent magnetic fields in present laboratories [49]. It is in accord with the Biot–Savart law (2.35), i.e., the strongest magnetic fields are induced for large charges $q$, small radii $R_{-1}$, and short periods $\tau_I$. 
2.3 Quantum Switching the Directions of Ring Currents and Magnetic Fields

Our previous experience (Sect. 2.2) offers a natural basis for extensions from quantum switching-on and -off to switching the direction of a ring current and the induced magnetic field in a model system, by means of the circularly polarized re-optimized $\pi$ laser pulse and (b) the resulting population dynamics of the ground $|X{1}A_{1g}\rangle$ and various excited $|n{1}E_{u+}\rangle$ ($n = 2, 4, 5$) states of Mg-porphyrin indicating optimal but not perfect population transfer from $|X{1}A_{1g}\rangle$ to $|5{1}E_{u+}\rangle$ (adapted from [28]).
are several times shorter than the durations $\tau_{\text{ori}}$ or $\tau_{\text{ali}}$ for orientation or alignment, then they can be fired with time delays $\Delta t = t_p$ and $2t_p$ for (third) dump and (fourth) pump laser pulses, respectively, during the same periods $\tau_{\text{ori}}$ or $\tau_{\text{ali}}$; else one has to wait at least for the next rotational revivals, which will provide again the scenario of pre-oriented or -aligned systems (if required). In the subsequent quantum simulations, we shall present the results using the time delays $\Delta t = t_p$ and $2t_p$ for (third) dump and (fourth) pump laser pulses, respectively, with the understanding that larger time delays will be applied, if necessary, in order to satisfy the requirements of suitable pre-orientations or -alignments. By reversibility of time and helicity, the effect of the (third) dump pulse (with re-optimized phase) is simply to switch-off the pre-excited ring current and induced magnetic field. Subsequently, the (fourth) pump pulse will switch it on again, but with opposite directionality, due to the reversed helicity of the dump and pump pulses. Obviously, the net effect of the (third) dump and (fourth) pump pulses is to change the directionality of the ring currents and induced magnetic fields. Applications of the concept to the model systems He$^+$ and FHF$^-$ are demonstrated in Figs. 2.8 and 2.9, respectively, see also the figure legends.

The primary effects of the left circularly polarized re-optimized $\pi$ pulse (second pulse) is the population transfer from the ground state to the left polarized state $|2p_+\rangle$ or $|1^{-1}\rangle$ of He$^+$ or FHF$^-$, respectively. Subsequently, the left and right circularly polarized dump and pump pulses (third and fourth pulses) transfer populations predominantly from the excited state back to the ground state, and then to the excited state with opposite magnetic or pseudorotational quantum numbers, i.e., $|2p_+\rangle$ or $|1^1\rangle$ of He$^+$ or FHF$^-$, respectively. The corresponding switches of the ring currents are obvious from the time evolutions of the mean values of the angular momentum or bending quantum numbers $\langle l(t) \rangle$ or $\langle v_b(t) \rangle$, and from the magnetic or pseudorotational quantum numbers $\langle m(t) \rangle$ or $\langle l(t) \rangle$, respectively. Finally, the switch-on and subsequent switch-off the directions of the magnetic fields $B_{Z,\text{He}}(t)$ and $B_{Z,F}(t)$ at the nuclei of the He$^+$ ion and at centers of F nuclear ring currents follow closely the time evolutions of the ring currents as monitored by the mean values of the quantum numbers $-\langle m(t) \rangle$ (due to negative electron charge) and $\langle l(t) \rangle$, respectively. The equivalent net effect has been achieved by E.K.U. Gross and coworkers using optimal laser pulses, with application to quantum switches of ring current in a nanoring model [20]. For an alternative approach to magnetic field switching in parallel quantum dots, see [86].

2.4 Conclusions

The progresses which are documented in Sects. 2.2 and 2.3 are stimulating. First, they provide useful criteria for systematic searches for systems which should allow to switch-on or -off, or to switch the directions of magnetic fields induced by ring currents, by means of well designed left or right circularly polarized re-optimized $\pi$ laser pulses. One important condition is that the chosen system should have proper
symmetry supporting degenerate states. In this respect, triply or more degenerate vibrational states, e.g., $T$-states of tetrahedral molecules, should be more advantageous than doubly degenerate states, e.g., $E$-states of planar molecules with $C_{nv}$ rotational axes ($n \geq 3$) because in first order (harmonic) approximation, it is not necessary to pre-orient or pre-align the system in order to generate nuclear ring currents. Second, according to the Biot–Savart law (2.35), one should look for a system with strong ring current $I$, i.e., with large charge $q$, with short period $\tau_I$.
Fig. 2.9 Quantum switching of pseudorotational nuclear ring currents and induced magnetic fields of the aligned FHF$^-$ anion, by means of a series of pump, dump, and pump re-optimized $\pi$ laser pulses with left, left, and right circular polarizations, respectively (see text). (a) Laser intensities; (b) populations of ground and excited states $|v_i\rangle$; (c) mean values of bending $\langle v_b(t) \rangle$ (gray solid) and pseudorotational quantum numbers $\langle l(t) \rangle$ (gray dashed) as well as $Z$-components of induced magnetic fields $B_{Z,F}$ at centers of F nuclear ring currents (black solid).

(2.32), and with small radius of the ring current $R_{-1}$ (2.34). The criteria for large charges and small radii point to pseudorotating heavy nuclei, and the criterion for short periods $\tau_I$ suggests corresponding high vibrational frequencies of the triply degenerate vibrational modes. Putting all criteria together, the tetrahedral molecule UH$_4$, for example, should be an ideal candidate because it possesses triply degenerate vibrational $T_2$ states (antisymmetric modes) with high vibrational (experimental) frequency, $\omega_a/(2\pi c) = 1484$ cm$^{-1}$ [87, 88] corresponding to $\tau_I = 22.5$ fs, and
the nucleus of the U atom carries a very high charge as well as very heavy mass such that it will carry out pseudorotations with very small radius. By approximate extrapolation of the present result for CdH₂ \( (B_{Z,Cd} = 318 \, \text{T}) \) at the center of the Cd nuclear ring current, the corresponding induced magnetic fields in UH₄ may approach 1,000 T! One may ask whether such huge fields could have feedbacks on the geometric or electronic structures of the molecule; we anticipate that this will not be the case because the very strong induced magnetic fields are typically localized in very small areas inside the mean ring current radii, without any major effect on the rest of the molecule.

Another challenge is to monitor the predicted laser driven quantum switches of ring currents and induced magnetic fields experimentally. The recent three-dimensional imaging of the corresponding toroidal structures of atoms carrying ring currents, carried out by the group of T. Baumert [29], is indeed encouraging for this purpose. In addition, one may consider and possibly extend the techniques which have already been applied successfully to analogous but much weaker effects which are induced by external magnetic fields [44–48]. Effects of magnetic fields induced by ring currents on nuclear magnetic resonance (NMR) spectra, such as chemical shifts, have already been predicted by L. Pauling [89], e.g., for aromatic molecules, and confirmed experimentally [90,91]. Extensions to the present quantum switching of these effects by means of laser pulses will be quite demanding because traditional NMR techniques would call for sufficiently long switching durations and life times of the ring currents, as well as sufficiently high densities of the samples (S. Glaser, private communication, 2009). As an alternative, we suggest to apply the option of ultrafast switch-on and -off, or switching the directionality of the rather huge magnetic fields, in particular within the rather small ring current radii of pseudorotating nuclei, to control the deflection of neutrons. This possibility is supported by recent work by Läuchli et al. [92], with references in particular to the extension from neutron scattering of orbital currents with translational symmetry [93,94] to broken [95] symmetry, see also, on one hand, the recent neutron experiments [96] indicating the presence of magnetic moments, compatible with the translation-invariant pattern of currents predicted by Varma [94], and on the other hand to Kerr effect measurements [97] showing evidence of time-reversal symmetry breaking (quoted from [92]). It would open entirely new possibilities for ultrafast analysis and control of chemical processes, by means of well-defined, pulsed interactions of molecules with neutrons. For example, the present approach would allow to design a series of circularly polarized re-optimized \( \pi \) laser pulses which switch on and off the ring currents and induced magnetic fields during very short periods, from attoseconds to picoseconds (depending on the model system). As a consequence, the induced magnetic fields could deflect a neutron beam such that it sweeps over a sample during these short periods. The deflected neutrons could then transfer momentum directly to the nuclei of the molecules in the sample, thus starting selected coherent vibrations or reactions, e.g., in the electronic ground state, see e.g., [98,99], during well-defined periods which are controlled by laser pulses.
Acknowledgements

We should like to express our gratitude to all co-authors, partners, and friends, Dr. Nadia Elghobashi-Meinhardt (Heidelberg), Prof. Leticia González (Jena), Dr. Markus Kitzler (Wien), Prof. Caroline Lasser (München), Mr. Guillermina Pérez-Hernández (Jena), Dr. Peter Sebald (Insheim), Prof. Tamar Seideman (Evanston), Dr. Luis Serrano-Andrés (Valencia), Prof. Yasuteru Shigeta (Osaka), and Prof. Kiyoshi Yagi (Tokyo) for fruitful cooperation on this topic. Stimulating discussions with Prof. Ilya Averbukh (Rehovot/Santa Barbara), Prof. André D. Bandrauk (Sherbrooke/Santa Barbara), Prof. Thomas Baumert (Kassel), Prof. Jamal Berakdar (Halle), Mr. Timm Bredtmann (Berlin), Prof. Gerd Buntkowsky (Darmstadt), Dr. Stephan Chelkowski (Sherbrooke/Santa Barbara), Prof. Paul B. Corkum (Ottawa), PD Dr. José R. Crespo López-Urrutia (Heidelberg), Dr. Chantal Daniel (Strasbourg), Prof. Dennis J. Diestler (Lincoln), Prof. Fahrad H.M. Faisal (Bielefeld), Prof. Yuichi Fujimura (Sendai), Prof. Steffen Glaser (München/Santa Barbara), Mr. Thomas Grohmann (Berlin), Prof. Eberhard K.U. Gross (Halle/Santa Barbara), Dr. Zoltán Harman (Heidelberg), Prof. Hirohiko Kono (Sendai), Prof. Shiro Koseki (Osaka), Dr. Andreas Läuchli (Lausanne), Monika Leibscher PhD (Berlin), PD Dr. Albrecht Lindinger (Berlin), Prof. Beate Paulus (Berlin), Dr. Sergey Patchkovskii (Ottawa/Santa Barbara), Prof. Trond Saue (Strasbourg), Dr. Torsten Siebert (Berlin), Dr. Olga Smirnova (Berlin/Santa Barbara), Prof. Anthony F. Starace (Lincoln/Santa Barbara), Prof. Alain Strich (Strasbourg), Mr. David Sulzer (Strasbourg), Prof. Kazuo Takatsuka (Tokyo), Prof. Joachim Ullrich (Heidelberg), Prof. Christoph van Wüllen (Kaiserslautern), PD Dr. Matthias Wollenhaupt (Kassel), Prof. Ludger Wöste (Berlin), and Prof. Klaas A. Zachariasse (Göttingen) are also gratefully acknowledged. We also thank Prof. Misha Yu. Ivanov (London/Santa Barbara) and Prof. David Tannor (Rehovot/Santa Barbara) for organizing the workshop on “Quantum Control of Light and Matter” at the Kavli Institute for Theoretical Physics (KITP) of the University of California at Santa Barbara (UCSB), providing wonderful scientific environment, Prof. David Gross (Santa Barbara) and his staff for all hospitality, and Mr. Dominik Sattler (Berlin) and Mr. Axel Schild (Berlin) for preparing movies and snapshots for quantum switching of nuclear ring currents. On this occasion, we should also like to thank the interpreters Oya Ataman, Kathleen Bieling, Silke Brendel-Evan, Sabine Goßner, Christjane Kreuter, Carola Otto, and Ralf Wiebel who helped to translate and communicate the topic from German sign language to English and vice versa during the workshop and other meetings over several years. Above all, we thank our wives Tanja and Etsuko for understanding and supporting our passion for science. Generous financial support by Deutsche Forschungsgemeinschaft DFG (project Sfb 450 TPC1, previously also GK788 and Ma 515/23-1), Agentur für Arbeit Berlin-Nord, and by Fonds der Chemischen Industrie is also gratefully acknowledged. This research was supported in part by the National Science Foundation under Grant No. PHY05-51164.

References

I. Barth and J. Manz

53. S.A. Rice, M. Zhao, Optical Control of Molecular Dynamics (Wiley, New York, 2000)
59. S.A. Rice, M. Zhao, Optical Control of Molecular Dynamics (Wiley, New York, 2000)