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Beyond the dipole approximation for helium and hydrogen in intense laser fields

K J Meharg, J S Parker and K T Taylor

Department of Applied Mathematics and Theoretical Physics, The Queen's University of Belfast, Belfast BT7 1NN, UK

E-mail: k.taylor@qub.ac.uk

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Abstract

We present a practical and efficient computational method for the solution of the time-dependent full-dimensionality Schrödinger equation for two-electron atoms in intense laser fields. The method, incorporating electric quadrupole and magnetic dipole terms, is a generalization of an approach within the dipole approximation that has previously found successful application at wavelengths from the visible to the XUV. We discuss the computational demands of non-dipole calculations for helium. We deduce from our helium formulation the equivalent formulation for hydrogen and report calculations we have performed on this atom beyond the dipole approximation, producing results that are found to be in good agreement with literature values obtained by a different method.

1. Introduction

The electric dipole approximation has been assumed valid in all of our previous work [1–7] on laser interactions with atoms and molecules. However, it is known that as one progresses to x-ray wavelengths this approximation loses its validity for outer-shell electrons, and indeed for any wavelength, extremely high intensity radiation will bring non-dipole Hamiltonian terms into play. This paper is concerned therefore with an initial exploration of the added theoretical and computational complexity such non-dipole terms bring about in the treatment of two-electron atoms. Focus is on the non-relativistic regime, and in particular the non-dipole terms arising through higher order contributions to the vector potential $\mathbf{A}(\mathbf{r}, t)$ experienced by each electron at position $\mathbf{r}$ are considered.

In the dipole approximation one assumes that the wavelength λ of the radiation is much larger than the distances over which the atomic wavefunction typically extends (that is $|k\mathbf{r}| \ll 1$, where $|k| = \omega/c = 2\pi/\lambda$) and so it is valid to make the approximation, $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$, which results in a vector potential $\mathbf{A}$ independent of spatial coordinates. This therefore amounts to neglecting the effects of the magnetic field $\mathbf{B}$ on the electron dynamics,

as well as approximating the role of the electric field $\mathcal{E}$ by retaining only its most dominant interaction term (i.e. one only takes into account the electric dipole interaction). The dipole approximation will break down as one moves to higher intensities and shorter wavelengths, and indeed, the failure of this approximation has already been investigated for hydrogen in the relativistic regime, through the use of various theoretical models (such as classical Monte Carlo simulations [8, 9] and reduced-dimensionality Dirac models [10]). Several groups have also investigated the effect of non-dipole terms in the non-relativistic regime, for the laser-driven hydrogen atom and hydrogen-like ions and have been able to see ranges of wavelengths and intensities where relativistic effects are still negligible, but the magnetic field effects significantly alter the electron dynamics. Different methods have been employed including: classical Monte Carlo simulations [11]; numerical integration of the time-dependent Schrödinger equation in two spatial dimensions [12–14]; three-dimensional calculations based on the strong field approximation [15, 16]; three-dimensional calculations based on Cartesian grids [17]; and three-dimensional calculations based on basis set methods [18]. On the other hand, up to now there has been only one published formulation for ionization of helium treated beyond the dipole approximation [19]. In that pioneering work, only two-dimensional motion of each electron was considered and electron exchange was neglected.

Our approach here is to incorporate the magnetic dipole and electric quadrupole interactions (of the order v/c), in order to make possible investigation of the validity of the dipole approximation for helium (and two-electron positive ions) within the non-relativistic regime (effects of the order $(v/c)^2$ are not included) and within our full-dimensionality treatment of electron motion.

The following section will therefore consider the description of the vector potential $\mathbf{A}(\mathbf{r}, t)$, that is an integral part of the analysis employed. A further section will address the general formulation of our full-dimensionality solution to the time-dependent Schrödinger equation for helium interacting with intense laser radiation, taking non-dipole terms into account in the laser–atom interaction Hamiltonian. The fourth section considers the computational demands of the corresponding calculations for helium in full-dimensionality and establishes that the calculation is feasible at XUV wavelengths but not yet at visible wavelengths. The fifth section deduces the corresponding theoretical formulation for the hydrogen atom in intense laser fields, and this is used to perform sample calculations yielding results that can be compared with literature values.

2. The vector potential

To establish the notation used in the following sections, we begin with a review of the dipole approximation. Assuming the laser field to be linearly polarized, the general form of the vector potential is:

$$\mathbf{A}(\mathbf{r}, t) = f(t) \cos(\mathbf{k} \cdot \mathbf{r} - \omega t + \delta_\omega) \hat{\mathbf{e}}, \quad (1)$$

where $\hat{\mathbf{e}}$ is the fixed direction of polarization of the radiation, ω is the photon energy, $\mathbf{k}$ is the propagation vector, with $|\mathbf{k}| = 2\pi/\lambda = \omega/c$, δ_ω is the phase and $f(t)$ is a slowly varying function of time on the scale of one cycle.

Within the dipole approximation, $e^{i\mathbf{k} \cdot \mathbf{r}} \approx 1$, and the vector potential therefore takes the following form:

$$\mathbf{A}(\mathbf{r}, t) \rightarrow \mathbf{A}^{(0)}(t) = f(t) \cos(\omega t - \delta_\omega) \hat{\mathbf{e}}. \quad (2)$$

Expanding $e^{i\mathbf{k} \cdot \mathbf{r}}$:

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 1 + (i\mathbf{k} \cdot \mathbf{r}) + \frac{1}{2!}(i\mathbf{k} \cdot \mathbf{r})^2 + \dots \quad (3)$$

and retaining the first two terms, the vector potential can be written:

$$\begin{aligned} \mathbf{A}(\mathbf{r}, t) &\rightarrow \frac{1}{2}f(t)[(1 + i\mathbf{k} \cdot \mathbf{r})e^{i(-\omega t + \delta_\omega)} + (1 - i\mathbf{k} \cdot \mathbf{r})e^{-i(-\omega t + \delta_\omega)}]\hat{\mathbf{e}} \\ &= f(t)[\cos(\omega t - \delta_\omega) + \mathbf{k} \cdot \mathbf{r} \sin(\omega t - \delta_\omega)]\hat{\mathbf{e}} \\ &= \mathbf{A}^{(0)}(t) + \mathbf{A}^{(1)}(\mathbf{r}, t), \end{aligned} \quad (4)$$

where $\mathbf{A}^{(0)}(t)$ is the previously obtained vector potential within the dipole approximation, while, $\mathbf{A}^{(1)}(\mathbf{r}, t)$ is a correction term, taking into account the momentum of the photons, of order v/c smaller than $\mathbf{A}^{(0)}(t)$,

$$\mathbf{A}^{(1)}(\mathbf{r}, t) = (\mathbf{k} \cdot \mathbf{r})f(t) \sin(\omega t - \delta_\omega)\hat{\mathbf{e}}. \quad (5)$$

Taking the laser polarization axis in the z direction, and the propagation vector is in the x direction, we have:

$$\mathbf{A}^{(0)}(t) = A^{(0)}(t)\hat{\mathbf{z}} = f(t) \cos(\omega t - \delta_\omega)\hat{\mathbf{z}}, \quad (6)$$

and,

$$\mathbf{A}^{(1)}(\mathbf{r}, t) = -\frac{x}{c} \frac{dA^{(0)}}{dt} \hat{\mathbf{z}}. \quad (7)$$

The inclusion of $\mathbf{A}^{(1)}(\mathbf{r}, t)$ in $\mathbf{A}(\mathbf{r}, t)$ enables the modelling of the electron dynamics to order v/c , and corresponds to taking into account the magnetic dipole and electric quadrupole interactions. In the electric dipole approximation, where the vector potential is spatially independent, the magnetic field $\mathbf{B}$ is zero, and the electric field is approximated by

$$\mathcal{E} \rightarrow -\frac{1}{c} \frac{dA^{(0)}(t)}{dt}. \quad (8)$$

However, on retaining the additional term $\mathbf{A}^{(1)}(\mathbf{r}, t)$, the electric and magnetic fields are given by

$$\mathcal{E} \rightarrow -\frac{1}{c} \frac{\partial}{\partial t} (A^{(0)}(t) + \mathbf{A}^{(1)}(\mathbf{r}, t)), \quad (9)$$

and

$$\mathbf{B} \rightarrow \nabla \times \mathbf{A}^{(1)}(\mathbf{r}, t). \quad (10)$$

3. Helium theory

In all formulations so far of our full-dimensionality theoretical treatment of the time-dependent Schrödinger equation for the helium atom in intense laser fields we have only gone so far as to treat the electron–laser interaction within the dipole approximation. In the dipole approximation the overall magnetic quantum number M of the system is conserved and indeed, if the atom is initially in its ground state, M remains conserved at the value zero. In consequence, our previously published formulations of the theory have been restricted to specifically the $M = 0$ special case. Since, as we shall see below, the non-dipole terms break the conservation of M , we take the opportunity in this section to not only formulate expressions for matrix elements involving these non-dipole terms, but also to establish expressions for matrix elements of the other M -conserving Hamiltonian terms for arbitrary M value.

We begin below by setting out the various Hamiltonian terms we will consider in going beyond the dipole approximation. This is followed by sub-sections establishing the wavefunction form and the set of two-dimensional time-dependent radial equations that ensue from our mixed finite-difference/basis set formulation of the helium wavefunction. Subsequent sub-sections formulate matrix elements for the various distinct terms forming the Hamiltonian.

3.1. The Hamiltonian

In going beyond the dipole approximation the Hamiltonian for a two-electron atom interacting with a linearly polarized laser pulse is now extended to include terms up to order v/c . Thus:

$$\begin{aligned}
 H(t) = & -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}} - \frac{i}{c}[\mathbf{A}^{(0)}(t) + \mathbf{A}^{(1)}(\mathbf{r}_1, t)] \cdot \nabla_1 \\
 & + \frac{1}{2c^2}|\mathbf{A}^{(0)}(t) + \mathbf{A}^{(1)}(\mathbf{r}_1, t)|^2 - \frac{i}{c}[\mathbf{A}^{(0)}(t) + \mathbf{A}^{(1)}(\mathbf{r}_2, t)] \cdot \nabla_2 \\
 & + \frac{1}{2c^2}|\mathbf{A}^{(0)}(t) + \mathbf{A}^{(1)}(\mathbf{r}_2, t)|^2,
 \end{aligned} \tag{11}$$

where Z is the charge of the nucleus, $[\mathbf{A}^{(0)}(t) + \mathbf{A}^{(1)}(\mathbf{r}_i, t)]$ is the vector potential of the laser field depending on the position of electron i , and $\mathbf{r}_1$ and $\mathbf{r}_2$ are the positions of each of the electrons.

Some of the terms in the above expression can be removed. Firstly, the spatially independent contributions:

$$\frac{1}{2c^2}|\mathbf{A}^{(0)}(t)|^2 \quad \text{and} \quad \frac{1}{2c^2}|\mathbf{A}^{(0)}(t)|^2$$

can be dropped through a well-known unitary transformation of the wavefunction, while the contributions:

$$\frac{1}{2c^2}|\mathbf{A}^{(1)}(\mathbf{r}_1, t)|^2 \quad \text{and} \quad \frac{1}{2c^2}|\mathbf{A}^{(1)}(\mathbf{r}_2, t)|^2$$

can be ignored since they make a contribution only at the relativistic level— $|\mathbf{A}^{(1)}(\mathbf{r}_i, t)|^2$ is of order $(v/c)^2$ smaller than $\mathbf{A}^{(0)}(t)$. We also choose to drop the terms

$$-\frac{i}{c}\mathbf{A}^{(1)}(\mathbf{r}_1, t) \cdot \nabla_1 \quad \text{and} \quad -\frac{i}{c}\mathbf{A}^{(1)}(\mathbf{r}_2, t) \cdot \nabla_2.$$

This is because we have found such terms to contribute in a negligible fashion to results (reported below) we have obtained for the hydrogen atom in intense laser fields. They have also been dropped by others [18] investigating hydrogen. Thus:

$$H(t) = H_{\text{at}} + H_{\text{ee}} + H_{\text{int}} + H_{\text{ndip}}, \tag{12}$$

where the terms H_{at} , H_{ee} , H_{int} and H_{ndip} of the Hamiltonian are, respectively, the atomic Hamiltonian

$$H_{\text{at}} = -\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2}, \tag{13}$$

the electron–electron repulsion Hamiltonian,

$$H_{\text{ee}} = \frac{1}{r_{12}} \tag{14}$$

and the laser interaction Hamiltonian (within the dipole approximation) is

$$H_{\text{int}} = -\frac{i}{c}\mathbf{A}^{(0)}(t) \cdot \nabla_1 - \frac{i}{c}\mathbf{A}^{(0)}(t) \cdot \nabla_2. \tag{15}$$

and the laser–atom interaction non-dipole correction contribution is

$$H_{\text{ndip}} = \frac{1}{c^2}\mathbf{A}^{(0)}(t) \cdot \mathbf{A}^{(1)}(\mathbf{r}_1, t) + \frac{1}{c^2}\mathbf{A}^{(0)}(t) \cdot \mathbf{A}^{(1)}(\mathbf{r}_2, t). \tag{16}$$

3.2. The wavefunction

As described previously e.g. [1], the angular dependence of the helium wavefunction is handled through a basis set expansion $|l_1 l_2 L M\rangle$ of coupled spherical harmonics. The inclusion of extra non-dipole terms in the Hamiltonian means a range of M values must be retained. The wavefunction therefore takes the form:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} |l_1 l_2 L M\rangle, \quad (17)$$

where

$$|l_1 l_2 L M\rangle = (-1)^{l_2 - l_1 - M} \sum_{m_1, m_2} \sqrt{2L+1} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} |l_1 m_1\rangle |l_2 m_2\rangle, \quad (18)$$

where $|l_i m_i\rangle$ are one-electron spherical harmonics, and the linear combination of products is specified through a 3- j symbol.

3.3. The coupled radial equations

Through the orthonormality of the angular basis $|l_1 l_2 L M\rangle$, one obtains a set of coupled two-dimensional radial equations for the functions $F_{l'_1 l'_2 L' M'}(r_1, r_2, t)$:

$$i \frac{\partial}{\partial t} F_{l'_1 l'_2 L' M'}(r_1, r_2, t) = r_1 r_2 \langle l'_1 l'_2 L' M' | H \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} |l_1 l_2 L M\rangle, \quad (19)$$

where H is given by equation (12). We now consider evaluation of matrix elements involving these Hamiltonian terms in turn.

3.4. The radial atomic Hamiltonian

The contribution due to the atomic Hamiltonian is of the form

$$I_{\text{at}} = r_1 r_2 \langle l'_1 l'_2 L' M' | \left(-\frac{1}{2} \nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2} \nabla_2^2 - \frac{Z}{r_2} \right) \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} |l_1 l_2 L M\rangle. \quad (20)$$

Elementary operations allow us to simplify this contribution to the form

$$I_{\text{at}} = \sum_{j=1}^2 \left[-\frac{1}{2} \frac{\partial^2}{\partial r_j^2} + \frac{1}{2} \frac{l'_j(l'_j + 1)}{r_j^2} - \frac{Z}{r_j} \right] F_{l'_1 l'_2 L' M'}(r_1, r_2, t). \quad (21)$$

3.5. The radial dielectronic Hamiltonian

The contribution due to the dielectronic Coulomb repulsion term is of the form

$$I_{\text{ee}} = r_1 r_2 \langle l'_1 l'_2 L' M' | \left(\frac{1}{r_{12}} \right) \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} |l_1 l_2 L M\rangle. \quad (22)$$

This contribution can be reduced using the techniques of spherical algebra. This is done in appendix A yielding,

$$I_{\text{ee}} = \sum_{k=0}^{\infty} \frac{r_{\leq}^k}{r_{>}^{k+1}} \sum_{l_1, l_2, L, M} (-1)^{l_1 + l'_2 + L'} \delta_{L, L'} \delta_{M, M'} \times \left\{ \begin{matrix} l'_1 & l'_2 & L' \\ l_2 & l_1 & k \end{matrix} \right\} \langle l'_1 \| C_k \| l_1 \rangle \langle l'_2 \| C_k \| l_2 \rangle F_{l_1 l_2 L' M'}(r_1, r_2, t), \quad (23)$$

where $\langle l'_i \| C_k \| l_i \rangle$ are reduced matrix elements of a single tensor operator, and $\left\{ \begin{matrix} l'_1 & l'_2 & L' \\ l_2 & l_1 & k \end{matrix} \right\}$ are 6- j symbols.

3.6. The radial laser dipole interaction Hamiltonian

The contribution due to the laser interaction term (within the dipole approximation) is of the form

$$I_{\text{int}} = r_1 r_2 \langle l'_1 l'_2 L' M' | \sum_{j=1}^2 \left(-\frac{i}{c} \mathbf{A}^{(0)}(t) \cdot \nabla_j \right) \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} | l_1 l_2 L M \rangle. \quad (24)$$

This contribution can again be reduced using the techniques of spherical algebra. This is done in appendix B yielding,

$$\begin{aligned} I_{\text{int}} = & \sum_{j=1}^2 -\frac{i}{2c} A^{(0)}(t) \sum_{l_1, l_2, L, M} \left[2 \frac{\partial}{\partial r_j} + \frac{l_j(l_j+1) - l'_j(l'_j+1)}{r_j} \right] F_{l_1 l_2 L M}(r_1, r_2, t) \\ & \times (-1)^{l'_k - M'} [(2L' + 1)(2L + 1)(2l'_j + 1)(2l_j + 1)]^{1/2} \delta_{l_k, l'_k} \\ & \times \delta_{M, M'} \begin{pmatrix} l'_j & 1 & l_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & L & 1 \\ -M' & M' & 0 \end{pmatrix} \begin{Bmatrix} L' & L & 1 \\ l_j & l'_j & l'_k \end{Bmatrix}, \end{aligned} \quad (25)$$

where $k = \{2, 1\}$ for values of $j = \{1, 2\}$ respectively.

3.7. Non-dipole laser interaction contribution

The contribution to the radial equations from those terms in the Hamiltonian present as corrections to the laser interaction term is:

$$I_{\text{ndip}} = r_1 r_2 \langle l'_1 l'_2 L' M' | \sum_{j=1}^2 \left(\frac{1}{c^2} \mathbf{A}^{(0)}(t) \cdot \mathbf{A}^{(1)}(\mathbf{r}_j, t) \right) \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} | l_1 l_2 L M \rangle, \quad (26)$$

where $\mathbf{A}^{(0)}(t) = A^{(0)}(t) \hat{\mathbf{z}}$, and (see equation (7)),

$$\mathbf{A}^{(1)}(\mathbf{r}_j, t) = -\frac{x_j}{c} \frac{dA^{(0)}(t)}{dt} \hat{\mathbf{z}}. \quad (27)$$

This contribution has also been reduced in appendix C yielding,

$$\begin{aligned} I_{\text{ndip}} = & \frac{1}{\sqrt{2}} \sum_{j=1}^2 \frac{1}{c^2} A^{(0)}(t) \left[-\frac{1}{c} \frac{dA^{(0)}(t)}{dt} \right] \\ & \times \sum_{l_1, l_2, L, M} F_{l_1 l_2 L M}(r_1, r_2, t) r_j (-1)^{l'_k - M'} \delta_{l_k, l'_k} \begin{pmatrix} l'_j & 1 & l_j \\ 0 & 0 & 0 \end{pmatrix} \\ & \times [(2L + 1)(2L' + 1)(2l_j + 1)(2l'_j + 1)]^{1/2} \begin{Bmatrix} L' & L & 1 \\ l_j & l'_j & l'_k \end{Bmatrix} \\ & \times \left[\delta_{M, M'+1} \begin{pmatrix} L' & L & 1 \\ -M' & M & -1 \end{pmatrix} - \delta_{M, M'-1} \begin{pmatrix} L' & L & 1 \\ -M' & M & 1 \end{pmatrix} \right], \end{aligned} \quad (28)$$

where $k = \{2, 1\}$ for values of $j = \{1, 2\}$ respectively.

4. Computational demands of helium

In this section we discuss the factors that affect the computational cost of solving the two-electron Schrödinger equation in equation (19). Experience solving equation (19) in the dipole

approximation (i.e. with non-dipole terms in the interaction Hamiltonian discarded) enables us to estimate the computational cost of solving equation (19) in its full generality, and to specify the limits in which the numerical solution is feasible on presently available supercomputers.

Numerical solution of equation (19) in the dipole approximation has been discussed in detail elsewhere [1–7]. In this previous work the radial variables r_1 and r_2 are treated by finite-difference methods, and the same basis set decomposition described above is used to treat the angular variables. The elements of the basis set (also called states or partial waves in this work) are the coupled spherical harmonics $|l_1 l_2 L M\rangle$. The set is rendered finite by setting a maximum value $l_{\max}$ to l_1 and l_2 , and $M_{\max}$ to M . $L_{\max}$ is necessarily restricted to $2l_{\max}$. An acceptable value for $l_{\max}$ depends on both laser intensity and frequency, and can only be reliably determined through convergence testing during the process of numerical integration. We find for example that at XUV frequencies (say $\lambda < 10$ nm) a choice of $l_{\max} = 5$ is acceptable, and remains acceptable at intensities as high as 10^{17} W cm $^{-2}$. At optical wavelengths on the other hand (say $\lambda \sim 780$ nm) we use $l_{\max} = 24$ and must place an upper limit of about 1.6×10^{15} W cm $^{-2}$ on laser intensity.

When we attempt to solve equation (19) in its full generality we discover a dramatic increase in the computational cost compared to the equations within the dipole approximation. The overriding factor leading to this increase is the substantial increase in the size of the basis set: total angular momentum M is no longer conserved and thus a much larger number of partial waves $F_{l_1 l_2 L M}(r_1, r_2, t)$ need to be considered since now another label, M , must be run over. Again, in contrast to work within the dipole approximation where $l_1 + l_2 + L$ was restricted to be either even or odd, now both even and odd values must be allowed for.

In order to illustrate this dramatic increase in the size of the basis set, consider a sample basis set (really only appropriate to short wavelengths and low intensities) where the maximum value of $l_1 = l_2$ is 5 (i.e. $L_{\max} = 10$). Within the dipole approximation, and with the initial state the ground state of the atom, one need only consider those states of even parity $l_1 + l_2 + L$ satisfying $M = 0$. This results in the inclusion of 91 different states in the basis set. Retaining non-dipole terms and taking $M_{\max} = L_{\max} = 10$, one would find that 1296 states need to be retained in the basis set. Moreover, truncation of the set to a smaller number of values of M about 0, does not result in a significant decrease in the total number of states in the set, since the number of states pertaining to a particular M value decreases significantly as one considers values of M increasingly far from 0. For example, taking $M_{\max} = 5$ (i.e. including only those states with M in the range $[-5, 5]$) will only reduce the number of states from 1296 to 1156.

Another factor leading to an increase in computational demand on moving away from the dipole approximation is due to the number of states coupled to any one particular state. These couplings are due to the additional terms in the radial equations that need to be evaluated. This is best illustrated by again considering the sample basis set used above ($M_{\max} = L_{\max} = 10$, with 1296 states).

Figure 1 displays the possible couplings between the different states in the basis set. The presence of a filled point at a particular row–column intersection indicates that some form of coupling occurs between the two states, identified by their ID numbers. An explanation of each of the different forms of coupling will follow, however it is first important to point out how the states have been ordered in the basis set.

The states have been ordered in the basis set, so that in considering all the couplings between the different states, the difference in the ID numbers of the coupled states is kept to a minimum across the entire set, i.e. it gives rise to the banded form the matrix has in figure 1. The ordering of the states is therefore such that they have first been grouped according to their value of M , starting from $-M_{\max}$ up to $M_{\max}$. Each of the states within these groups are then

Figure 1. Couplings between different states in a basis where $l_{\max} = 5$, $M_{\max} = 10$ are indicated by filled points. Dashed lines mark the divisions along each axis between partial waves of differing M , over the range $M = -10$ to $M = 10$.

grouped according to their value of L and placed in order of increasing L , for each value of M . Finally the states of the same L and M , but differing l_1 and l_2 are grouped according to the parity of $l_1 + l_2 + L$ and then listed (first the even parity states followed by the odd). Therefore in figure 1, the dashed lines indicate the divisions between states of differing M values, starting from $M = -10$ and running up to $M = 10$, along each axis, and the square encircled shows the couplings between states whose value of $M = 0$ in each case.

In figure 1, the filled points in the outer extremities (involving a coupling between adjacent M values) arise from non-dipole terms. There are up to 24 partial waves that may couple to any one particular partial wave (due to these non-dipole terms), and so significantly more additional terms in the set of radial equations need to be evaluated. All other filled points in figure 1 occur within diagonal blocks, indicating that they involve fixed M . Within each diagonal block the filled points forming an outer envelope curve on both sides of the diagonal line arise from the dipole interaction term. Points closer to the diagonal line arise from the atomic and dielectronic Hamiltonian terms.

Figure 2 is a magnification of part of figure 1, illustrating the coupling between $M = 0$ states. There are 146 states for this value of M (of both even and odd parity), and in this figure the dashed lines indicate the divisions between states of differing L values, from $L = 0$ up to $L = 10$. As in the previous figure, the outer envelope points indicate coupling between states due to the dipole interaction. Note when $M = 0$ these terms result in the coupling of states of differing L , that is $L' = L \pm 1$ (up to a maximum of 8 states for any particular state). However, on closer examination of the coupling of other basis states when $M \neq 0$ (not shown), one sees that dipole coupling can also occur between states of the same L and M (but of course pertaining to differing values of l_1 and l_2). The coupling due to the electron–electron interaction term depends on the order retained in the $1/r_{12}$ expansion. The black points occurring within square blocks near and on the diagonal indicate the couplings necessary if terms up to order 2 are retained in the $1/r_{12}$ expansion, while the light grey points are the additional couplings required to retain terms in the $1/r_{12}$ expansion up to order 5. Note that

Figure 2. Magnification of figure 1, now indicating by filled points only the coupling between states where in each case $M = 0$. The dashed lines indicate the divisions along each axis between partial waves of differing L , over the range from $L = 0$ up to $L = 10$. In each L group, the even parity states are listed first, followed by the odd parity states.

the electron–electron interaction term will only allow the coupling of states with the same value of M and L that are also of the same $l_1 + l_2 + L$ parity. Furthermore, as the order of the $1/r_{12}$ expansion increases, more and more states tend to couple to any one particular state, of the same L , M and parity, until all possible states are coupled to.

As remarked above, in the limit of optical wavelengths ($\lambda \sim 780$ nm), a choice of $l_{\max} = 24$, $L_{\max} = 2l_{\max}$, $M_{\max} = 0$, defines a finite basis set of states $|l_1 l_2 L M\rangle$ that yields high-accuracy results provided we restrict ourselves to the dipole approximation. The number of states in this basis set is 5525. We have shown [7] that numerical solution of the two-electron Schrödinger equation (equation (19)) in the dipole approximation is straightforward on this basis set, but only at present on a high-end massively parallel supercomputer. If instead we attempt to solve equation (19) in its full generality, with $M_{\max}$ in the range 10 to 48, then the size of the basis set ranges from 200 000 to 400 000. This problem is beyond the scope of present computer technology.

In the limit of XUV wavelengths ($\lambda < 10$ nm), experience with the equations in the dipole approximation implies that $l_{\max} = 5$ and $L_{\max} = 2l_{\max}$ is more than sufficient for high accuracy solutions. If we choose $M_{\max} = 5$ for the non-dipole approximation case, then the basis set size is 1296 elements. The non-dipole Hamiltonian couples more of these basis elements to each other than does the Hamiltonian in the dipole approximation. We estimate that this greater degree of coupling doubles the amount of numerical computation. We conclude that in this limit the problem is tractable, but again, only on the highest performance computers presently available.

5. Hydrogen theory and calculation

The helium Hamiltonian contains many one-electron operators, including all of those describing the interaction between the laser field and the atom, which allows a

full-dimensionality theoretical treatment for hydrogen to be largely deducible from that set out for helium in section 3. Hydrogen also has the advantage that calculations for that atom beyond the dipole approximation are tractable on modern workstations whilst the corresponding helium calculations would require resources on the largest supercomputers, as discussed above. There are also calculations [18] in the literature for hydrogen using an alternative method that can provide data for comparison. Moreover, in hydrogen we can examine the relative importance of certain non-dipole terms. (This examination helps justify our neglect of certain non-dipole terms in our helium formulation.) Thus in the first sub-section below we set out briefly the hydrogen mathematical analysis and in the second we present results we have calculated for hydrogen that can be usefully compared with those in the literature.

5.1. Hydrogen theory

We can write the Hamiltonian for hydrogen beyond the dipole approximation as

$$H(t) = -\frac{1}{2}\nabla^2 - \frac{Z}{r} - \frac{i}{c}\mathbf{A}^{(0)}(t) \cdot \nabla - \frac{i}{c}\mathbf{A}^{(1)}(r, t) \cdot \nabla + \frac{1}{c^2}\mathbf{A}^{(0)}(t) \cdot \mathbf{A}^{(1)}(r, t), \quad (29)$$

where obviously the fourth and fifth terms are the non-dipole ones. We dropped terms analogous to the fourth one in our helium analysis above. Here we persist with both the fourth and the fifth but our results below will demonstrate the negligible contribution of the fourth.

The one-electron wavefunction form corresponding to the two-electron finite-difference/basis-set approach previously taken for helium is,

$$\Psi(r, t) = \sum_{l,m} \frac{1}{r} F_{l,m}(r, t) |l m\rangle, \quad (30)$$

where $|l m\rangle$ are spherical harmonics. Carrying through analysis similar to that for helium above we arrive at the following coupled set of one-dimensional radial equations,

$$\begin{aligned} i\frac{\partial}{\partial t} F_{l,m}(r, t) = & \left[-\frac{1}{2} \frac{\partial^2}{\partial r^2} + \frac{1}{2} \frac{l(l+1)}{r^2} - \frac{Z}{r} \right] F_{l,m} \\ & + \frac{i}{c} A^{(0)}(t) \left[D_m^l \left(-\frac{\partial}{\partial r} + \frac{l}{r} \right) F_{l-1,m} + D_m^{l+1} \left(-\frac{\partial}{\partial r} - \frac{(l+1)}{r} \right) F_{l+1,m} \right] \\ & + \frac{1}{c^3} A^{(0)}(t) \frac{dA^{(0)}}{dt} (E_{-m}^l r F_{l-1,m-1} - E_m^l r F_{l-1,m+1}) \\ & + \frac{1}{c^3} A^{(0)}(t) \frac{dA^{(0)}}{dt} (-E_{m-1}^{l+1} r F_{l+1,m-1} + E_{-m-1}^{l+1} r F_{l+1,m+1}) \\ & + \frac{i}{c^2} \frac{dA^{(0)}}{dt} G_{-m}^l \left[(1-2m)r \frac{\partial}{\partial r} - (2l^2 + 2l + m - 2) \right] F_{l,m-1} \\ & - \frac{i}{c^2} \frac{dA^{(0)}}{dt} G_m^l \left[(1+2m)r \frac{\partial}{\partial r} - (2l^2 + 2l - m - 2) \right] F_{l,m+1} \\ & + \frac{i}{c^2} \frac{dA^{(0)}}{dt} \left[-r \frac{\partial}{\partial r} + (l-1) \right] (H_{-m}^l F_{l-2,m-1} - H_m^l F_{l-2,m+1}) \\ & + \frac{i}{c^2} \frac{dA^{(0)}}{dt} \left[r \frac{\partial}{\partial r} + (l+2) \right] (H_{m-1}^{l+2} F_{l+2,m-1} - H_{-m-1}^{l+2} F_{l+2,m+1}), \end{aligned} \quad (31)$$

where the coefficients D_m^l , E_m^l , G_m^l , H_m^l have simple dependences on l and m , namely:

$$D_m^l = \left[\frac{(l-m)(l+m)}{(2l+1)(2l-1)} \right]^{1/2} \quad (32)$$

$$E_m^l = \frac{1}{2} \left[\frac{(l-m-1)(l-m)}{(2l+1)(2l-1)} \right]^{1/2} \quad (33)$$

$$G_m^l = \frac{1}{2} \frac{[(l-m)(l+m+1)]^{1/2}}{(2l+3)(2l-1)} \quad (34)$$

$$H_m^l = \frac{1}{2} \left[\frac{(l+m)(l-m)(l-m-1)(l-m-2)}{(2l+1)(2l-1)^2(2l-3)} \right]^{1/2}. \quad (35)$$

We note that the terms in equation (31) involving coefficients G_m^l and H_m^l arise from considering the term $-i/c \mathbf{A}^{(1)}(\mathbf{r}, t) \cdot \nabla$ in the Hamiltonian and bring about off-diagonal coupling in m and sometimes also in l . We further note that the terms involving coefficients E_m^l arise from considering the term $1/c^2 \mathbf{A}^{(0)}(t) \cdot \mathbf{A}^{(1)}(\mathbf{r}, t)$ in the Hamiltonian and bring about off-diagonal coupling in both l and m simultaneously. Finally the terms involving coefficients D_m^l arise from the dipole operator and involve merely unit change in l and no change in m .

The calculations reported below were accomplished by making appropriate changes to an existing code (previously limited to the dipole approximation) so that all the terms in the above equation were accounted for.

5.2. Hydrogen calculation

Ionization yields have already been calculated for hydrogen initially in the $2p_x$ state exposed to a Gaussian-profile laser pulse of width 5 cycles and frequency 0.5 au by Bugacov *et al* [18]. They carried out calculations within both the dipole approximation and beyond up to an intensity of $4.0 \times 10^{17} \text{ W cm}^{-2}$. The availability of these results prompted us to make the same choice of laser pulse parameters in these our first test calculations.

Bugacov *et al* [18] also solved the time-dependent Schrödinger equation numerically but their method differed from ours as follows. Firstly they made a further approximation in the Hamiltonian; in that they dropped the term $-i/c \mathbf{A}^{(1)}(\mathbf{r}, t) \cdot \nabla$. This is effectively the same as dropping the last six terms for each of the radial equations (31). They further perform a gauge transformation which shifts the canonical momentum and rotate the coordinate system about the y -axis. The wavefunction of [18] is represented by a basis set formed from linear combinations of $S_{nl}^\kappa(r) Y_{lm}(\theta, \phi)$, where $S_{nl}^\kappa(r)$ are radial Sturmian functions and $Y_{lm}(\theta, \phi)$ are spherical harmonics. Finally, their time propagation is based on the split-operator technique, whereas our code uses an Arnoldi propagator.

Results as given in [18] are illustrated in figure 3, with the results obtained in the present work also marked at the various intensities examined. The results we have obtained do appear in reasonable agreement with those obtained in [18]. The maximum ionization yield is found to occur around an intensity of $2 \times 10^{16} \text{ W cm}^{-2}$, in agreement with that found in [18]. The ionization yields obtained have been found insensitive to non-dipole corrections, up to intensities around $1.0 \times 10^{17} \text{ W cm}^{-2}$. This again is in agreement with the results in [18]. At the higher intensities, the ionization yields obtained are in general agreement with those of [18]; in that, as one goes to higher intensities it has been found that the yields obtained through using the dipole approximation increasingly depart from those found incorporating the non-dipole corrections. The yields obtained at intensities above $3 \times 10^{17} \text{ W cm}^{-2}$ do however appear to be lower than those obtained in [18], both within the dipole approximation, and through incorporating the further corrections.

It should be noted that in order to obtain these yields, a significant amount of computational time (on a personal computer) was required, mainly due to the large extent of radial space that had to be considered. For example, when the corrections are incorporated into the dipole

Figure 3. A comparison between results from Bugacov *et al* [18] and the present work showing how the ionization yield varies with peak intensity, for hydrogen, initially in the $2p_x$ state, driven by a Gaussian-profile laser pulse of width 5 cycles and frequency 0.5 au. The results of Bugacov *et al* within the dipole approximation are displayed as a solid black line, while those incorporating the corrections to the dipole approximation are given by a dashed black line. The results from the present work are also given; those marked by black crosses are the results within the dipole approximation, while those incorporating the corrections are given by black circles.

approximation a radial box of 90 au has been found sufficient at the lower intensities. However by an intensity of $2 \times 10^{17} \text{ W cm}^{-2}$ a radial box of around 1200 au was found to be required, increasing to around 2000 au for an intensity of $4 \times 10^{17} \text{ W cm}^{-2}$. The maximum value of l that needs to be retained in the wavefunction expansion (necessary for converged results) is 10, while the maximum magnitude of m is 5 for an intensity of $4 \times 10^{17} \text{ W cm}^{-2}$. Due to the large extent of the radial space, our results have been obtained using a rather coarse radial mesh spacing of $\delta r = 0.4 \text{ au}$.

Calculations have been performed, both retaining all the terms in the coupled radial equations (31), and dropping those due to the term $-i/cA^{(1)}(\mathbf{r}, t) \cdot \nabla$ in the Hamiltonian. It was found that the yields obtained across the range of intensities do not differ significantly whether these extra terms are retained or not. This thus validates the approximation of Bugacov *et al* to drop the contribution of $-i/cA^{(1)}(\mathbf{r}, t) \cdot \nabla$ in the Hamiltonian and motivates our dropping of the corresponding terms in our treatment of helium above.

6. Conclusion

We have given above a general formulation of the angular analysis underlying our established method for handling, in full-dimensionality and in spherical geometry, the time-dependent Schrödinger equation governing the behaviour of helium and helium-like ions exposed to intense laser fields. This general formulation allows non-dipole terms in the laser-atom interaction to be considered. The computational demands of these calculations have been considered in detail. We have deduced the corresponding analysis for the hydrogen atom exposed to intense laser fields and used this to make sample calculations yielding results in very good agreement with those from an alternative method.

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Appendix A

The contribution due to the dielectronic Coulomb repulsion term is of the form

$$I_{ee} = r_1 r_2 \langle l'_1 l'_2 L' M' | \left(\frac{1}{r_{12}} \right) \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} | l_1 l_2 L M \rangle. \quad (\text{A.1})$$

This contribution has been evaluated analytically, and details of this are given below.

The operator $1/r_{12}$ can be written in terms of Legendre polynomials $P_k(\cos \theta_{12})$ [20]

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \theta_{12}), \quad (\text{A.2})$$

where $r_{>} = \max\{r_1, r_2\}$, $r_{<} = \min\{r_1, r_2\}$ and θ_{12} is the angle contained between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$.

I_{ee} then becomes

$$I_{ee} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \sum_{l_1, l_2, L, M} \langle l'_1 l'_2 L' M' | P_k(\cos \theta_{12}) | l_1 l_2 L M \rangle F_{l_1 l_2 L M}(r_1, r_2, t). \quad (\text{A.3})$$

Further reduction of the matrix elements $\langle l'_1 l'_2 L' M' | P_k(\cos \theta_{12}) | l_1 l_2 L M \rangle$ is achieved using the spherical harmonic addition theorem [21], expressed in terms of Racah irreducible tensor operators C_k^m :

$$P_k(\cos \theta_{12}) = \sum_{m=-k}^k (-1)^m C_k^m C_k^{-m}, \quad (\text{A.4})$$

where

$$C_k^m = \left[\frac{4\pi}{(2k+1)} \right]^{1/2} Y_{km}. \quad (\text{A.5})$$

Now in general [22], the tensor product of two tensor operators is formed by the Clebsch–Gordan series:

$$C_j^m(j_1, j_2) = \sqrt{2j+1} \sum_{m_1, m_2} (-1)^{-j_1+j_2-m} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -m \end{pmatrix} C_{j_1}^{m_1} C_{j_2}^{m_2}, \quad (\text{A.6})$$

and so one sees that

$$\begin{aligned} C_0^0(k(\theta_1, \phi_1), k(\theta_2, \phi_2)) &= \sum_{m=-k}^k \begin{pmatrix} k & k & 0 \\ m & -m & 0 \end{pmatrix} C_k^m(\theta_1, \phi_1) C_k^{-m}(\theta_2, \phi_2) \\ &= \frac{(-1)^k}{\sqrt{2k+1}} P_k(\cos \theta_{12}), \end{aligned} \quad (\text{A.7})$$

through evaluation of the 3- j symbol. That is, $P_k(\cos \theta_{12})$ can be expressed in terms of a tensor product, whose matrix elements have been defined in Rotenberg *et al* [22], and so:

$$\begin{aligned} \langle l'_1 l'_2 L' M' | P_k(\cos \theta_{12}) | l_1 l_2 L M \rangle &= (-1)^k \sqrt{2k+1} (-1)^{L'-M'} \\ &\times \begin{pmatrix} L' & 0 & L \\ -M' & 0 & M \end{pmatrix} \langle l'_1 l'_2 L' || C_0(k(\theta_1, \phi_1), k(\theta_2, \phi_2)) || l_1 l_2 L \rangle, \end{aligned} \quad (\text{A.8})$$

where $\langle l'_1 l'_2 L' \| C_0(k(\theta_1, \phi_1), k(\theta_2, \phi_2)) \| l_1 l_2 L \rangle$ is the reduced matrix element of the tensor product, that is independent of M and M' , defined as

$$\langle l'_1 l'_2 L' \| C_0(k(\theta_1, \phi_1), k(\theta_2, \phi_2)) \| l_1 l_2 L \rangle = [(2L' + 1)(2L + 1)]^{1/2} \times \begin{Bmatrix} l'_1 & l'_2 & L' \\ l_1 & l_2 & L \\ k & k & 0 \end{Bmatrix} \langle l'_1 \| C_k(\theta_1, \phi_1) \| l_1 \rangle \langle l'_2 \| C_k(\theta_2, \phi_2) \| l_2 \rangle, \quad (\text{A.9})$$

where $\langle l' \| C_k \| l \rangle$ is a reduced matrix element of a single tensor operator given by

$$\langle l' \| C_k \| l \rangle = (-1)^{l'} [(2l' + 1)(2l + 1)]^{1/2} \begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}. \quad (\text{A.10})$$

There are several points to note about the expression for $\langle l'_1 l'_2 L' M' | P_k(\cos \theta_{12}) | l_1 l_2 L M \rangle$. Firstly, the presence of

$$\begin{pmatrix} L' & 0 & L \\ -M' & 0 & M \end{pmatrix} \quad (\text{A.11})$$

in the expression indicates that the angular integral will only be non-zero provided $L = L'$ and $M = M'$. Second, with $L = L'$ the 9- j symbol in the expression is actually proportional to a 6- j symbol:

$$\begin{Bmatrix} l'_1 & l'_2 & L \\ l_1 & l_2 & L \\ k & k & 0 \end{Bmatrix} = (-1)^{l'_2 + l_1 + L + k} \frac{1}{[(2L + 1)(2k + 1)]^{1/2}} \begin{Bmatrix} l'_1 & l'_2 & L \\ l_2 & l_1 & k \end{Bmatrix}. \quad (\text{A.12})$$

The matrix elements I_{ee} are therefore given by

$$I_{ee} = \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} \sum_{l_1, l_2, L, M} (-1)^{l_1 + l'_2 + L'} \delta_{L, L'} \delta_{M, M'} \times \begin{Bmatrix} l'_1 & l'_2 & L' \\ l_2 & l_1 & k \end{Bmatrix} \langle l'_1 \| C_k \| l_1 \rangle \langle l'_2 \| C_k \| l_2 \rangle F_{l_1 l_2 L' M'}(r_1, r_2, t), \quad (\text{A.13})$$

where the summation over all partial waves has been reduced to only those with the same value of L and M as the partial wave being considered, and valid values of l_1 and l_2 . Indeed, note that $(l_1 + l'_1 + k)$ and $(l_2 + l'_2 + k)$ must both be of even parity in order to ensure that the 3- j symbols defined within the reduced matrix elements (see equation (A.10)) are non-zero. Therefore these conditions, together with the triangular inequalities $\Delta(l_1 k l'_1)$ and $\Delta(l_2 k l'_2)$, determine the valid values of l_1 and l_2 for the partial waves coupling any particular wave. The total number of partial waves coupled by this contribution ultimately depends therefore on the number of terms N , retained in the series expansion of $1/r_{12}$ (or equivalently, the maximum value of k), since inevitably, as the range of k increases, so too would the possible range in l_1 and l_2 of the partial waves for which there would be non-zero contributions.

Appendix B

The contribution due to the laser interaction term (within the dipole approximation) is of the form

$$I_{\text{int}} = r_1 r_2 \langle l'_1 l'_2 L' M' | \sum_{j=1}^2 \left(-\frac{i}{c} \mathbf{A}^{(0)}(t) \cdot \nabla_j \right) \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} | l_1 l_2 L M \rangle. \quad (\text{B.1})$$

This expression may first be simplified using the relation

$$\nabla_j = \frac{1}{2} [\nabla_j^2, \mathbf{r}_j]. \quad (\text{B.2})$$

Now since $\mathbf{A}^{(0)}(t) = A^{(0)}(t)\hat{\mathbf{z}}$:

$$\mathbf{A}^{(0)}(t) \cdot \nabla_j = \frac{1}{2} A^{(0)}(t) [\nabla_j^2, r_j \cos \theta_j], \quad (\text{B.3})$$

and (for $j = 1, 2$)

$$\begin{aligned} & [\nabla_j^2, r_j \cos \theta_j] \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} |l_1 l_2 L M\rangle \\ &= \left[2 \frac{\cos \theta_j}{r_1 r_2} \frac{\partial}{\partial r_j} + \frac{1}{r_1 r_2} \left(r_j \cos \theta_j \frac{l_j^2}{r_j^2} - \frac{l_j^2}{r_j^2} r_j \cos \theta_j \right) \right] \\ &\quad \times F_{l_1 l_2 L M}(r_1, r_2, t) |l_1 l_2 L M\rangle, \end{aligned} \quad (\text{B.4})$$

and also

$$\langle l'_1 l'_2 L' M' | \cos \theta_j l_j^2 | l_1 l_2 L M \rangle = l_j(l_j + 1) \langle l'_1 l'_2 L' M' | \cos \theta_j | l_1 l_2 L M \rangle \quad (\text{B.5})$$

$$\langle l'_1 l'_2 L' M' | l_j^2 \cos \theta_j | l_1 l_2 L M \rangle = l'_j(l'_j + 1) \langle l'_1 l'_2 L' M' | \cos \theta_j | l_1 l_2 L M \rangle \quad (\text{B.6})$$

the contribution I_{int} becomes

$$\begin{aligned} I_{\text{int}} &= \sum_{j=1}^2 -\frac{i}{2c} A^{(0)}(t) \sum_{l_1, l_2, L, M} \left[2 \frac{\partial}{\partial r_j} + \frac{l_j(l_j + 1) - l'_j(l'_j + 1)}{r_j} \right] F_{l_1 l_2 L M}(r_1, r_2, t) \\ &\quad \times \langle l'_1 l'_2 L' M' | \cos \theta_j | l_1 l_2 L M \rangle. \end{aligned} \quad (\text{B.7})$$

The matrix elements $\langle l'_1 l'_2 L' M' | \cos \theta_j | l_1 l_2 L M \rangle$ can be evaluated using expansion (18) for $|l_1 l_2 L M\rangle$, so that for $j = 1$ say:

$$\begin{aligned} \langle l'_1 l'_2 L' M' | \cos \theta_1 | l_1 l_2 L M \rangle &= (-1)^{l'_2 - l'_1 - M' + l_2 - l_1 - M} [(2L' + 1)(2L + 1)]^{1/2} \\ &\quad \times \sum_{m'_1, m'_2} \sum_{m_1, m_2} \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & -M' \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \\ &\quad \times \int Y_{l'_1 m'_1}^* \sqrt{\frac{4\pi}{3}} Y_{1,0} Y_{l_1 m_1} d\Omega_1 \int Y_{l'_2 m'_2}^* Y_{l_2 m_2} d\Omega_2. \end{aligned} \quad (\text{B.8})$$

Evaluation of these integrals involving products of two or three spherical harmonics then gives:

$$\begin{aligned} \langle l'_1 l'_2 L' M' | \cos \theta_1 | l_1 l_2 L M \rangle &= (-1)^{-l'_1 - l_1} \delta_{l_2, l'_2} \delta_{M, M'} \begin{pmatrix} l'_1 & 1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times \sum_{m'_1, m'_2} (-1)^{-m'_1} [(2L' + 1)(2L + 1)(2l'_1 + 1)(2l_1 + 1)]^{1/2} \\ &\quad \times \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & -M' \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m'_1 & m'_2 & -M' \end{pmatrix} \begin{pmatrix} l'_1 & 1 & l_1 \\ -m'_1 & 0 & m'_1 \end{pmatrix}, \end{aligned} \quad (\text{B.9})$$

where the summations over m'_1 and m'_2 are constrained to values where $m'_1 + m'_2 = M'$ (in order for the product of 3- j symbols to be non-zero). Note also that for $j = 1$, this component of the Hamiltonian only couples partial waves with the same l_2 and M values as the wave being considered.

The final step in the evaluation of the matrix elements $\langle l'_1 l'_2 L' M' | \cos \theta_j | l_1 l_2 L M \rangle$ utilizes equation (2.20) of Rotenberg *et al* [22] which provides a relation between products of 3- and

6-*j* symbols. Applying this relation to the following product of a 3- and 6-*j* symbol, one therefore obtains (together with utilization of the symmetry properties of the 3-*j* symbol):

$$\begin{pmatrix} L' & L & 1 \\ -M' & M' & 0 \end{pmatrix} \left\{ \begin{matrix} L' & L & 1 \\ l_1 & l'_1 & l'_2 \end{matrix} \right\} = (-1)^{l_1+l'_1+l'_2-M'} \sum_n (-1)^n \begin{pmatrix} l'_1 & 1 & l_1 \\ -n & 0 & n \end{pmatrix} \\ \times \begin{pmatrix} l'_1 & l'_2 & L' \\ n & M'-n & -M' \end{pmatrix} \begin{pmatrix} l_1 & l'_2 & L \\ n & M'-n & -M' \end{pmatrix} \quad (\text{B.10})$$

and so it is evident that

$$\langle l'_1 l'_2 L' M' | \cos \theta_1 | l_1 l_2 L M \rangle = (-1)^{l'_2-M'} [(2L'+1)(2L+1)(2l'_1+1)(2l_1+1)]^{1/2} \\ \times \delta_{l_2, l'_2} \delta_{M, M'} \begin{pmatrix} l'_1 & 1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & L & 1 \\ -M' & M' & 0 \end{pmatrix} \left\{ \begin{matrix} L' & L & 1 \\ l_1 & l'_1 & l'_2 \end{matrix} \right\}. \quad (\text{B.11})$$

In considering this matrix element we see that it will only be non-zero when $l_1 = l'_1 \pm 1$, $l_2 = l'_2$, $M = M'$ and $L = L'$, $L' \pm 1$ (similarly for the second electron, with the roles of l_1 and l_2 interchanged).

Note however that for $M = 0$, the constraints on the value of L increase so that the matrix element given by expression (B.11) is only non-zero when $L = L' \pm 1$ (due to the properties of the 3-*j* symbols). This is the standard case encountered for the atom initially in its ground state and working within the dipole approximation. Therefore, within the dipole approximation (with M conserved at $M = 0$) the overall parity of $l_1 + l_2 + L$ is the same for all the partial waves (if one considers this contribution, together with each of the other terms in the Hamiltonian— I_{at} and I_{ee} , their coupling is only between states where the parity of $l_1 + l_2 + L$ is the same as that of the initial state).

The contribution due to the laser interaction term (within the dipole approximation) is therefore of the following form:

$$I_{\text{int}} = \sum_{j=1}^2 -\frac{i}{2c} A^{(0)}(t) \sum_{l_1, l_2, L, M} \left[2 \frac{\partial}{\partial r_j} + \frac{l_j(l_j+1) - l'_j(l'_j+1)}{r_j} \right] F_{l_1 l_2 L M}(r_1, r_2, t) \\ \times (-1)^{l'_k-M'} [(2L'+1)(2L+1)(2l'_j+1)(2l_j+1)]^{1/2} \delta_{l_k, l'_k} \\ \times \delta_{M, M'} \begin{pmatrix} l'_j & 1 & l_j \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L' & L & 1 \\ -M' & M' & 0 \end{pmatrix} \left\{ \begin{matrix} L' & L & 1 \\ l_j & l'_j & l'_k \end{matrix} \right\}, \quad (\text{B.12})$$

where $k = \{2, 1\}$ for values of $j = \{1, 2\}$ respectively.

Appendix C

The contribution to the radial equations from those terms in the Hamiltonian present as corrections to the laser interaction term is:

$$I_{\text{ndip}} = r_1 r_2 \langle l'_1 l'_2 L' M' | \sum_{j=1}^2 \left(\frac{1}{c^2} \mathbf{A}^{(0)}(t) \cdot \mathbf{A}^{(1)}(\mathbf{r}_j, t) \right) \sum_{l_1, l_2, L, M} \frac{F_{l_1 l_2 L M}(r_1, r_2, t)}{r_1 r_2} | l_1 l_2 L M \rangle, \quad (\text{C.1})$$

where $\mathbf{A}^{(0)}(t) = A^{(0)}(t) \hat{\mathbf{z}}$, and (see equation (7)),

$$\mathbf{A}^{(1)}(\mathbf{r}_j, t) = -\frac{x_j}{c} \frac{dA^{(0)}(t)}{dt} \hat{\mathbf{z}}. \quad (\text{C.2})$$

This contribution can be evaluated analytically, and details are given below.

Substituting for $A^{(0)}(t)$ and $A^{(1)}(r_j, t)$ we see that

$$I_{\text{ndip}} = \sum_{j=1}^2 \frac{1}{c^2} A^{(0)}(t) \left[-\frac{1}{c} \frac{dA^{(0)}(t)}{dt} \right] \times \sum_{l_1, l_2, L, M} \langle l'_1 l'_2 L' M' | r_j \sin \theta_j \cos \phi_j | l_1 l_2 L M \rangle F_{l_1 l_2 L M}(r_1, r_2, t). \quad (\text{C.3})$$

Therefore in order to evaluate I_{ndip} , one first needs to evaluate the matrix elements $\langle l'_1 l'_2 L' M' | r_j \sin \theta_j \cos \phi_j | l_1 l_2 L M \rangle$ for $j = 1, 2$. The procedure that has been used to evaluate this is summarized below for the case $j = 1$.

The coordinate $x_1 = r_1 \sin \theta_1 \cos \phi_1$ is first expressed in terms of spherical harmonics:

$$r_1 \sin \theta_1 \cos \phi_1 = -r_1 \frac{1}{2} \sqrt{\frac{8\pi}{3}} [Y_{11}(\theta_1, \phi_1) - Y_{1-1}(\theta_1, \phi_1)]. \quad (\text{C.4})$$

The matrix element is then expanded out fully in terms of spherical harmonics to obtain

$$\begin{aligned} & \langle l'_1 l'_2 L' M' | r_1 \sin \theta_1 \cos \phi_1 | l_1 l_2 L M \rangle \\ &= -\frac{1}{2} \sqrt{\frac{8\pi}{3}} r_1 (-1)^{l'_2 - l'_1 - M' + l_2 - l_1 - M} [(2L' + 1)(2L + 1)]^{1/2} \\ & \times \sum_{m'_1, m'_2} \sum_{m_1, m_2} \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & -M' \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} \\ & \times \int Y_{l'_1 m'_1}^*(\theta_1, \phi_1) [Y_{11}(\theta_1, \phi_1) - Y_{1-1}(\theta_1, \phi_1)] Y_{l_1 m_1}(\theta_1, \phi_1) d\Omega_1 \\ & \times \int Y_{l'_2 m'_2}^*(\theta_2, \phi_2) Y_{l_2 m_2}(\theta_2, \phi_2) d\Omega_2. \end{aligned} \quad (\text{C.5})$$

Both of these integrals can be easily evaluated and one obtains

$$\begin{aligned} & \langle l'_1 l'_2 L' M' | r_1 \sin \theta_1 \cos \phi_1 | l_1 l_2 L M \rangle = -\frac{1}{\sqrt{2}} r_1 (-1)^{l'_1 - M' - l_1 - M} \\ & \times [(2L' + 1)(2L + 1)(2l'_1 + 1)(2l_1 + 1)]^{1/2} \delta_{l'_2 l_2} \begin{pmatrix} l'_1 & 1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \\ & \times \sum_{m'_1, m'_2} \sum_{m_1} (-1)^{-m'_1} \begin{pmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & -M' \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m'_2 & -M \end{pmatrix} \\ & \times \left[\begin{pmatrix} l'_1 & 1 & l_1 \\ -m'_1 & 1 & m_1 \end{pmatrix} - \begin{pmatrix} l'_1 & 1 & l_1 \\ -m'_1 & -1 & m_1 \end{pmatrix} \right]. \end{aligned} \quad (\text{C.6})$$

The matrix element is therefore composed of products of four 3- j symbols. Note that the combination of these 3- j symbols means that limitations are put on the summations over m_1 , m'_1 , and m'_2 —the only non-zero terms are those where $m_1 = m'_1 \pm 1$ and $m'_2 = M' - m'_1 = M - m_1$.

Using equation (2.20) of [22] to re-express combinations of 3- j symbols in terms 3- j and 6- j symbols one obtains,

$$\begin{aligned} & \begin{pmatrix} L' & L & 1 \\ -M' & M' - 1 & 1 \end{pmatrix} \begin{Bmatrix} L' & L & 1 \\ l_1 & l'_1 & l'_2 \end{Bmatrix} = (-1)^{l_1 + l'_1 + l'_2 - M' + 1} \sum_n (-1)^n \begin{pmatrix} l'_1 & l'_2 & L' \\ n & M' - n & -M' \end{pmatrix} \\ & \times \begin{pmatrix} l_1 & l'_2 & L \\ n - 1 & M' - n & -M' + 1 \end{pmatrix} \begin{pmatrix} l'_1 & 1 & l_1 \\ -n & 1 & n - 1 \end{pmatrix} \end{aligned} \quad (\text{C.7})$$

and so one obtains (for $j = 1$ say):

$$\begin{aligned} \langle l'_1 l'_2 L' M' | r_1 \sin \theta_1 \cos \phi_1 | l_1 l_2 L M \rangle &= \frac{1}{\sqrt{2}} r_1 (-1)^{l'_2 - M'} \delta_{l_2, l'_2} \begin{pmatrix} l'_1 & 1 & l_1 \\ 0 & 0 & 0 \end{pmatrix} \\ &\times [(2L + 1)(2L' + 1)(2l_1 + 1)(2l'_1 + 1)]^{1/2} \begin{Bmatrix} L' & L & 1 \\ l_1 & l'_1 & l'_2 \end{Bmatrix} \\ &\times \left[\delta_{M, M'+1} \begin{pmatrix} L' & L & 1 \\ -M' & M & -1 \end{pmatrix} - \delta_{M, M'-1} \begin{pmatrix} L' & L & 1 \\ -M' & M & 1 \end{pmatrix} \right]. \end{aligned} \quad (\text{C.8})$$

One therefore sees that this term of the Hamiltonian brings in coupling between partial waves with $L = L'$, $L' \pm 1$, and $M = M' \pm 1$, adding greatly to the complexity of the problem.

Therefore,

$$\begin{aligned} I_{\text{ndip}} &= \frac{1}{\sqrt{2}} \sum_{j=1}^2 \frac{1}{c^2} A^{(0)}(t) \left[-\frac{1}{c} \frac{dA^{(0)}(t)}{dt} \right] \\ &\times \sum_{l_1, l_2, L, M} F_{l_1 l_2 L M}(r_1, r_2, t) r_j (-1)^{l'_k - M'} \delta_{l_k, l'_k} \begin{pmatrix} l'_j & 1 & l_j \\ 0 & 0 & 0 \end{pmatrix} \\ &\times [(2L + 1)(2L' + 1)(2l_j + 1)(2l'_j + 1)]^{1/2} \begin{Bmatrix} L' & L & 1 \\ l_j & l'_j & l'_k \end{Bmatrix} \\ &\times \left[\delta_{M, M'+1} \begin{pmatrix} L' & L & 1 \\ -M' & M & -1 \end{pmatrix} - \delta_{M, M'-1} \begin{pmatrix} L' & L & 1 \\ -M' & M & 1 \end{pmatrix} \right], \end{aligned} \quad (\text{C.9})$$

where $k = \{2, 1\}$ for values of $j = \{1, 2\}$ respectively.

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