Electric dipole moments of lithium atoms in Rydberg states*

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Recently, the diverse properties of Rydberg atoms, which probably arise from its large electric dipole moment (EDM), have been explored. In this paper, we report electric dipole moments along with Stark energies and charge densities of lithium Rydberg states in the presence of electric fields, calculated by matrix diagonalization. Huge electric dipole moments are discovered. In order to check the validity of the EDMs, we also use these electric dipole moments to calculate the Stark energies by numerical integration. The results agree with those calculated by matrix diagonalization.

Keywords: electric dipole moment, Stark energy, charge density, matrix diagonalization

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1. Introduction

Rydberg atoms are a topic of growing interest in research worldwide. For example, Ditzhuijzen *et al.*[1] observed spatially resolved dipole–dipole interaction between Rydberg atoms. Schauß *et al.*[2] experimentally demonstrated the potential of Rydberg gases to generate exotic phases of matter. Peyronel *et al.*[3] obtained quantum nonlinearity by coherent coupling of propagating photons to strongly interacting atomic Rydberg states in a cold, dense atomic gas. We have studied many properties and processes of Rydberg atoms, such as level shifts due to the Stark effect,[4–7] state transfer,[8,9] Autler–Townes splitting,[10] and electromagnetically induced transparency.[11] Many unique features of Rydberg states have been discovered recently, such as the dipole blocking effect,[1] spatially ordered distribution,[2] and strong interaction between atoms.[3] These characteristics are closely related to the electric dipole moments (EDMs). One often calculates the EDMs according to the polarizability, based on the second-order perturbation theory[12–14] for weak electric fields. In this article, we report numerical calculations of Rydberg state-selective of EDMs, wavefunctions, charge densities, and Stark energies of lithium atoms by matrix diagonalization. This method is applicable for both weak and strong fields. In order to confirm the validity of the calculated EDMs, we also use these values to calculate the Stark energies by numerical integration.

2. Electric dipole moments, charge distributions, and stark energies calculated by matrix diagonalization

The present calculations are carried out in terms of atomic unit. The Schrödinger equation for the valence electron of the Li atom in an electric field is

$$(-\nabla^2/2 + V(r) + \boldsymbol{F}\cdot\boldsymbol{r})\Psi = W\Psi, \tag{1}$$

where $-\nabla^2/2 + V(r)$ is the Hamiltonian operator for zero field, $\boldsymbol{F}$, $\boldsymbol{r}$, and $\boldsymbol{F}\cdot\boldsymbol{r}$ represent the electric field vector, the radial vector, and the interaction energy between the electric field and the electric dipole, respectively. The effective core potential $V(r)$ accounts for the interaction between the electron and the nucleus shielded by the two core electrons. For large distances r, $V(r)$ approaches the Coulomb interaction $-1/r$. Deviations of $V(r)$ from the Coulomb interaction at short distances are parameterized in terms of quantum defects. Here, W is the eigenvalue of the energy, and Ψ is the wavefunction of the resulting Stark state. In order to calculate the EDMs of Stark states, for example with principle and magnetic quantum numbers $n = 8$ and $m = 0$, we first solve the Schrödinger equation without field numerically and select the wavefunctions with quantum numbers $6 \le n \le 11$ and $m = 0$ as basis functions Φ. Then we calculate the matrix elements of the interaction between the field and the dipole $\langle\Phi|\boldsymbol{F}\cdot\boldsymbol{r}|\Phi'\rangle$, set up the Hamiltonian in matrix representation and perform matrix diagonalization to obtain the energy eigenvalues and wavefunctions of the Stark states. Further details can be found in Refs. [15]–[17]. The calculations are carried out on a grid of

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electric fields, with step size $|\Delta \boldsymbol{F}| = 10$ V·cm^{-1}. The resulting lithium Stark structure in the vicinity of $n = 8$, $m = 0$ is shown in Fig. 1 (solid lines). At zero field, the two states with quantum numbers $n = 8$, $m = 0$, and $l = 0$ as well as $l = 1$ are non-degenerate with the remaining multiplet labeled by $n = 8$, $m = 0$, and $l = 2, 3, \ldots, 7$ because they have rather large quantum defects 0.3996 and 0.0539, respectively. The quantum defect for $l = 2$ is much smaller (about 0.002), which makes it almost degenerate with the remaining states ($l = 3, \ldots, 7$), which have zero quantum defects. For increasing field strength, the quantum numbers $l = 0, \ldots, 7$ correlate with the quantum numbers of the Stark components $n_1 = 0, \ldots, 7$, respectively.[15] Apparently, in the presence of low fields (below 4×10^4 V·cm^{-1}), the $n = 8$, $m = 0$ degenerate states ($2 \leq l \leq 7$) exhibit the linear Stark effect; the 8s and 8p states generate the quadratic Stark effect. In this limit, it is appropriate to use perturbation theory to calculate Stark state-selective polarizabilities, EDMs and Stark energies. However, when the electric field exceeds 4×10^4 V·cm^{-1}, the most rapidly increasing component of the $n = 8$ manifold approaches the most rapidly decreasing component of the $n = 9$ manifold. The interaction between them is so strong that the perturbation theory is no longer appropriate. Hence we have to employ a numerical method such as matrix diagonalization in order to calculate the properties of Li Rydberg atoms ($n = 8$, $m = 0$) in strong electric fields.

In order to understand the subsequent results for the EDMs, it is first helpful to know the effect of the electric field on the charge distributions Ψ^2 of Rydberg states. Exemplarily, we consider z-polarized electric fields. As a consequence, the electron probability distribution Ψ^2 has the z axis as a cylindrical symmetry axis. Hence the x and y components of the EDMs are equal to zero. Figure 2 shows the electron probability density distributions of the valence electron of the lithium atom in the Stark state with quantum numbers $n = 8$, $m = 0$, $n_1 = 0$ in the field of 0, 2×10^4, and 5×10^4 V·cm^{-1}. Apparently, the electron distribution in zero field is isotropic so that the atom does not have any natural dipole moment. At 2×10^4 and 5×10^4 V·cm^{-1}, the Rydberg atom is weakly and strongly polarized, respectively, with the electron driven preferably towards the negative z-axis.

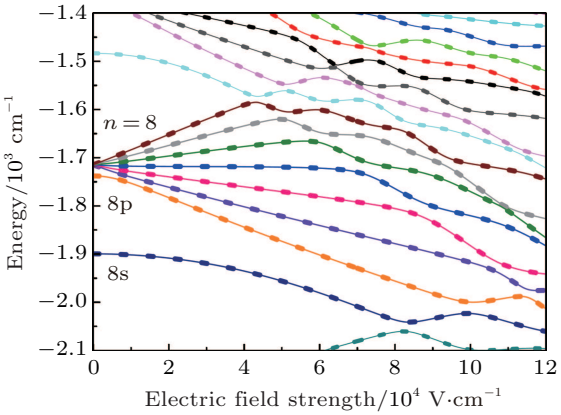


Fig. 1. (color online) Stark structure of atomic lithium Rydberg states near $n = 8$, $m = 0$. The solid lines are calculated by matrix diagonalization, on a grid of field strengths with step size $|\Delta \boldsymbol{F}| = 10$ V· cm^{-1}. The dots are calculated by numerical integration using the dipole moments.

The polarization characteristics of Rydberg atoms in external fields are usually described in terms of state-selective polarizabilities. For weak fields, these are robust i.e., they are approximately constant. In intense fields, the interaction between the external field and the Rydberg electron is large, and when it becomes comparable to the internal Coulomb interaction, the polarizabilities vary strongly with field strength. It is, therefore, no longer appropriate to use constant polarizabilities to describe the atomic polarization in intense fields. Here we can use the numerical results for the quantum mechanical EDMs $-e\langle\Psi|z|\Psi\rangle$ directly to express the degree of atomic polarization in z polarized fields. The negative sign indicates that the direction of EDM is parallel to the z polarized electric field. Figure 3 shows the calculated results, for the same step size that has been used in Fig. 1, $|\Delta \boldsymbol{F}| = 10$ V·cm^{-1} for z polarized fields. In general, all EDMs vary with the external field. Specially, the EDMs for $n_1 = 0$ and $n_1 = 1$ correspond to the Rydberg states, which have large quantum defects in zero

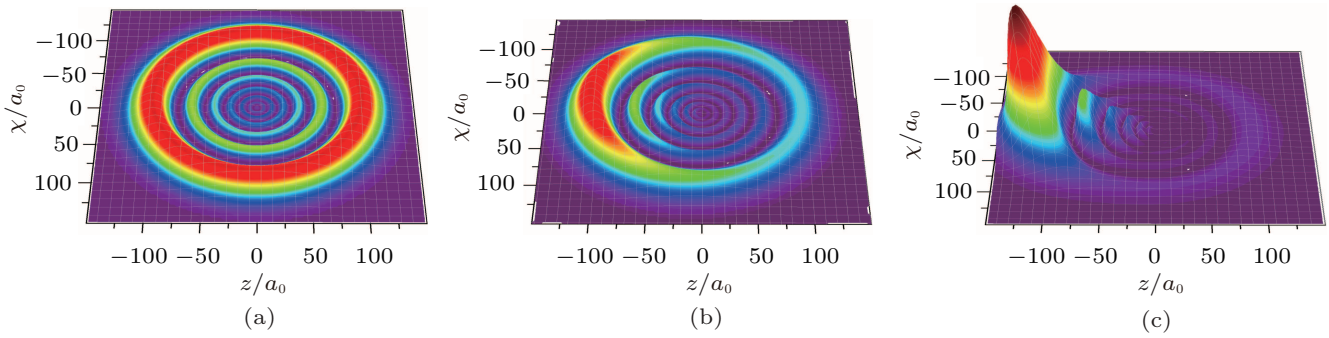


Fig. 2. (color online) The electronic probability density of atomic lithium in the Rydberg state with quantum numbers $n = 8$, $m = 0$, $n_1 = 0$, (a) $E = 0$ V·cm^{-1}, (b) $E = 2 \times 10^4$ V· cm^{-1}, (c) $E = 5 \times 10^4$ V·cm^{-1}, in the x–z plane. The density for $E = 0$ V·cm^{-1} is isotropic (a), the others have cylindrical symmetry with respect to the z axis ((b) and (c)). The coordinate perpendicular to the x–z plane is used as the scale for the quantity $r^2\Psi^2$;[18,19] the same absolute scales are used in panels (a)–(c). For presentations of the same relative scales $r^2\Psi^2$/max ($r^2\Psi^2$), we employ the same color codes in panels (a)–(c).

field, cf., Fig. 1, so they are quite different from the other EDMs. For $n_1 = 0$, the EDM increases linearly. For $n_1 = 1$, the linear increase at low fields slows down at larger fields. For $n_1 = 2$, the EDM increases rapidly to a maximum value 67.11 $e \cdot a_0$ as the field increases from 0 V·cm^{-1} to 1200 V·cm^{-1}. This implies a rather large polarizability in this domain of rather low fields. When the field increases beyond 1200 V·cm^{-1}, the EDM decreases slowly, implying small negative polarizability. For $n_1 = 3$, the EDM reaches a rather large value (61.37 $e \cdot a_0$) already at the first step of the field strength, 10 V·cm^{-1}, followed by a rapid decrease as the field increases till about 400 V·cm^{-1}; this implies negative polarizability with a rather large absolute value in this field domain. Beyond 400 V·cm^{-1}, the rate of decrease of the EDM slows down to approximately the same value as for $n_1 = 2$. The evolutions of the EDMs for $n_1 = 4, 5, 6, 7$ versus field strength are essentially parallel to the EDM for $n_1 = 3$, with systematic down shifts by about 30 $e \cdot a_0$, cf., Fig. 3. The "initial" value of the EDM for $n_1 = 7$ at the first step, 10 V·cm^{-1} is thus equal to -62.50 $e \cdot a_0$. The phenomenon of giant EDMs has been discovered previously also for Rydberg states of hydrogen atoms.[18,19] Here we emphasize for "Small field strengths, even infinitesimal field strength", the giant electric dipole moment.

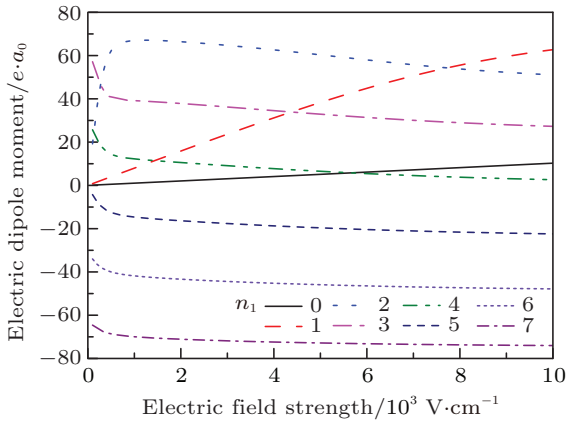


Fig. 3. (color online) The z component of electric dipole vs z-polarized electric field for the state of $n = 8$, $m = 0$, $n_1 = 0$, 1, 2, 3, 4, 5, 6, 7, with steps of 10 V·cm^{-1}.

3. Stark energies based on electric dipole moments

In order to verify the validity of the EDMs calculated by diagonalizaion, we calculate the Stark energies based on the EDMs to test their consistency with the energies obtained by matrix diagonalization. The interaction energy between the EDM $d_z = -e\langle\Phi|z|\Phi\rangle$ and the z-polarized electric field F_z is

$$W = -\int d_z \mathrm{d}F_z, \tag{2}$$

or in differential form

$$\mathrm{d}W = -d_z \mathrm{d}F_z. \tag{3}$$

Replacing infinitesimal changes $\mathrm{d}F_z$ by small finite changes, ΔF_z yields the approximation

$$\Delta W = -d_z \Delta F_z. \tag{4}$$

Here, d_z represents the EDM in the field F_z, and ΔF_z is the change of the electric field, also called the field step, and ΔW is the change of the energy due to ΔF_z. The Stark energy is calculated recursively by the following equation:

$$W_{i+1} = W_i + \Delta W, \tag{5}$$

which provides a numerical approximation to the integral equation (2) — it will be called "the integration method". In order to demonstrate the performance of this method, we calculate the Stark energy of the state with quantum numbers $n = 8$, $m = 0$, $n_1 = 0$, as an example. In practice, we increase the field step by step by ΔF_z; for each step, we calculate the change $\Delta W = -d_z \Delta F_z$ of the Stark energy; finally, the Stark energy W at field strength F_z is obtained by the approximation equation (5) to the Eq. (2). Figure 4 shows the integrated Stark energies for decreasing values of the field step $\Delta F_z = 10^4$, 10^3, 10^2, and 10 V·cm^{-1}. Apparently, the results converge to the reference values, which have been obtained by matrix diagonalization. The corresponding absolute or relative deviations between the Stark energies obtained by the two methods decrease from approximately 0.1 cm^{-1} to 0.001 cm^{-1}, or from 10^{-3} to 10^{-6}, respectively. Figure 5 shows the convergence of the average relative deviation upon decreasing field steps — the dependence of the deviation on ΔF_z is almost linear. Figure 1 compares the analogous results obtained by matrix diagonalization and by integration, using $\Delta F_z = 10$ V·cm^{-1}, for all Stark states with quantum numbers $n = 8$, $m = 0$, and neighbouring ones. The agreement appears to be perfect.

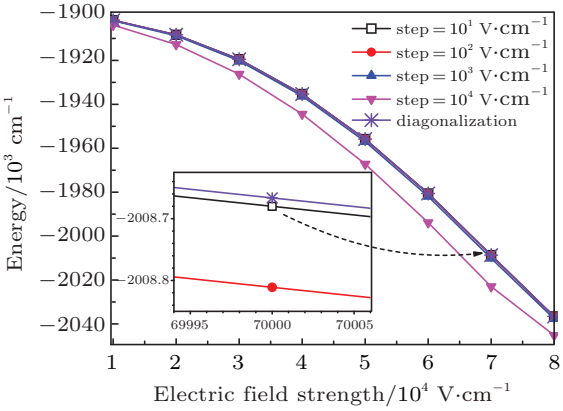


Fig. 4. (color online) The energies of the Stark state with quantum numbers $n = 8$, $m = 0$, and $n_1 = 0$ calculated by matrix diagonalization and by the integration method with field steps of 10 V·cm^{-1}, 10^2 V·cm^{-1}, 10^3 V·cm^{-1}, and 10^4 V·cm^{-1}, respectively. The convergence demonstrates the validity of the underlying electric dipole moments.

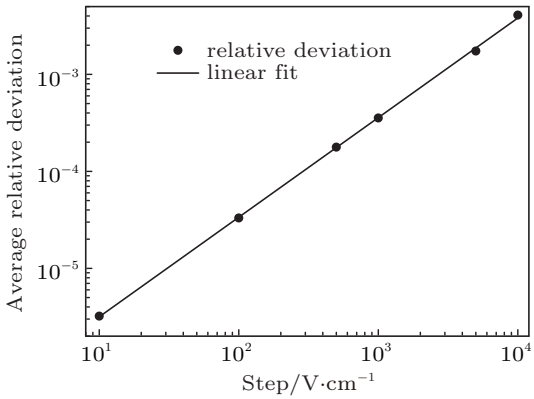


Fig. 5. The average relative deviation of the results obtained by matrix diagonalization and by integration versus electric field step. The black dots are calculated data, and the blue line is a linear fit.

4. Conclusions

We have calculated the z-components of electric dipole moments of atomic lithium in Rydberg states in z-polarized electric fields, exemplarily for quantum numbers $n = 8$, $m = 0$, $n_1 = 0, 1, \ldots, 6, 7$. For the specific case $n = 8$, $m = 0$, $n_1 = 0$, the linear increase of the EDM with increasing field strength has been rationalized in terms of the underlying systematic shifts of the electronic probability distributions induced by the external electric fields. In general, the EDMs may vary non-linearly with electric fields. Rydberg atoms in rather "small" electric fields, of the order of about 10 V·cm^{-1}, may exhibit huge EDMs, of the order of 60 $e \cdot a_0$. This may be closely related to the new phenomena of dipole blockade, spatially ordered structures (or so-called super atoms), and strong interactions between Rydberg atoms. In order to test the validity of the EDMs, we have calculated the related Stark energies by means of two methods. The first is diagonalization of the Hamilton matrix expressed in terms of field free basis functions. This yields the Stark energies together with the wavefunctions of the Rydberg states in the external fields. The wavefunctions are then used to calculate the non-vanishing z-components EDMs. The second method is the so-called integration method, it calculates the Stark energies as integrals of the z components of the EDMs integrated over the field strength. Numerical implementation of the method yields rapid convergence, with linear dependence on the field step which is used for integration. Excellent agreement of the Stark energies calculated by the two methods demonstrates the consistency of the methods, and the validity of the underlying EDMs not only for weak electric fields but also for strong ones.

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