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Corrections to atomic ground state energy due to interaction between atomic electric quadrupole and optical field*

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We study the ground state energy of an atom interacting with an oscillating optical field with electric dipole and quadrupole coupling. Under the rotating wave approximation, we derive the effective atomic Hamiltonians of the dipole/quadrupole coupling term within the perturbation theory up to the second order. Based on the effective Hamiltonians, we analyze the atomic ground-state energy corrections of these two processes in detail. As an application, we find that for alkali-like atoms, the energy correction from the quadrupole coupling is negligible small in comparison with that from the dipole coupling, which justifies the so-called dipole approximation used in literatures. Some special cases where the quadrupole interaction may have considerable energy corrections are also discussed. Our results would be beneficial for the study of atom–light interaction beyond dipole approximation.

Keywords: cold atom physics, quantum optics, atom-light interaction, electric quadrupole

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1. Introduction

The research on the interactions between electromagnetic field and matter plays a centre role in the progress of contemporary physics. A fundamental startpoint is to consider the coupling between atom and light, which is responsible for many physical phenomena. For example, the light emission and absorption of atoms and molecules are powerful sources to detect the underlying atomic structures and dynamic processes. It also enables us to manipulate the atomic internal and external degrees of freedom with the atom–light coupling, to realize states near or far from the thermodynamic equilibrium.[1–4]

The physics of ultracold atoms focuses on coherent quantum motion of atoms in the ultra-low temperature and many-body effects in these quantum gases due to the interaction between atoms.[5–8] Interaction between atoms and laser lights plays an important role in controlling cold atom systems, ranging from matured technologies such as laser cooling, optical trapping, and optical lattices to the latest developments such as synthetic gauge field and stimulated Raman adiabatic passage to achieve the ground state polar molecules.[9–13] In most of the studies in cold atom physics, the atom–light interaction is treated in the frame of dipole approximation which refers to the interaction between atomic electric dipole and the laser light, while the electric quadrupole interaction effect is usually neglected. It was shown that the rarely considered atomic electric quadrupole may lead to fractional frequency shifts in an optical lattice clock.[14–17] Nevertheless, the corrections there are estimated in the harmonic oscillator approximation and the general result brought by the electric quadrupole interaction is not clear. Especially, in what circumstances the electric quadrupole interaction may play a critical role and cannot be neglected is a question. In this paper to address this problem, we go beyond the harmonic approximation and take into account the dipole and quadrupole interactions on an equal foot.

The rest of this paper is organized as follows. In Section 2, we present the general formalism of atom–light coupling, and derive the effective Hamiltonians for the electric dipole and quadrupole interaction in a perturbative way, respectively. Then based on the results, we analyze the ground-state energy corrections for both processes in Section 3. Finally in Section 4, we give a brief summary.

2. Formalism and effective Hamiltonians

It is well known from a textbook of classical electrodynamics that, if a localized charge distribution described by $\rho(\boldsymbol{r})$ is placed in an external potential $\Phi(\boldsymbol{r})$, the electrostatic energy of the system is:[18]

$$H = \int \rho(\boldsymbol{r})\Phi(\boldsymbol{r})\mathrm{d}^3 r. \tag{1}$$

If the potential Φ is slowly varying over the region where $\rho(\boldsymbol{r})$ is noneligible, then it can be expanded as a Taylor series

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around a suitably chosen origin, which is

$$\Phi(\boldsymbol{r}) = \Phi(0) + \boldsymbol{r}\cdot\nabla\Phi(0) + \frac{1}{2}\sum_i\sum_j r_i r_j \frac{\partial^2\Phi}{\partial r_i \partial r_j}(0) + \cdots. \quad (2)$$

Utilizing the definition of the electric field $\boldsymbol{E} = -\nabla\Phi$ and taking $\nabla\cdot\boldsymbol{E} = 0$, equation (2) can be rewritten as

$$\begin{aligned}\Phi(\boldsymbol{r}) &= \Phi(0) - \boldsymbol{r}\cdot\boldsymbol{E}(0) \\ &\quad - \frac{1}{6}\sum_i\sum_j (3r_i r_j - r^2\delta_{ij})\frac{\partial E_j}{\partial r_i}(0) + \cdots. \end{aligned} \quad (3)$$

Substituting $\Phi(\boldsymbol{r})$ into Eq. (1), the energy H becomes

$$H = q\Phi(0) - \boldsymbol{p}\cdot\boldsymbol{E}(0) - \frac{1}{6}\sum_i\sum_j Q_{ij}\frac{\partial E_j}{\partial r_i}(0) + \cdots, \quad (4)$$

where $q = \int \rho(\boldsymbol{r}')\mathrm{d}^3 r'$ is the total charge, $\boldsymbol{p} = \int \boldsymbol{r}'\rho(\boldsymbol{r}')\mathrm{d}^3 r'$ is the dipole moment, and $Q_{ij} = \int (3r'_i r'_j - r'^2\delta_{ij})\rho(\boldsymbol{r}')\mathrm{d}^3 r'$ is the quadrupole moment. It can be seen that different multipoles interact with the external field in different characteristic ways, e.g., the charge with the potential, the dipole with the electric field, the quadrupole with the field gradient, and so on.

In general, due to the total charge of an atom is zero, the dipole term becomes the most important one in the atom–light interaction. In this paper, without loss of generality, we take an oscillatory light field $\boldsymbol{E}(t) = \sum_j \boldsymbol{e}_j E_j \cos(\boldsymbol{k}\cdot\boldsymbol{r} - \omega t + \phi_j)$ with vector component E_j and frequency ω, where $\boldsymbol{k}$ is the wave vector of the light field and ϕ_j is the initial phase. To facilitate the following discussions, we turn to the quantization description by replacing the observable quantities with the corresponding operators, and write the atom–light coupling Hamiltonian as $\hat{H}_{\mathrm{int}} = \hat{H}_{\mathrm{d}} + \hat{H}_{\mathrm{quad}} + \cdots$ with

$$\hat{H}_{\mathrm{d}} = -\hat{\boldsymbol{d}}\cdot\boldsymbol{E}(t), \quad (5)$$

$$\hat{H}_{\mathrm{quad}} = -\frac{1}{6}\sum_i\sum_j \hat{Q}_{ij}\frac{\partial E_j(t)}{\partial r_i}. \quad (6)$$

Here $\hat{\boldsymbol{d}} = -e\sum_\alpha \hat{\boldsymbol{r}}_\alpha$ is the electric dipole operator, $\hat{Q}_{ij} = -e\sum_\alpha(3(\hat{r}_\alpha)_i(\hat{r}_\alpha)_j - \hat{r}_\alpha^2\delta_{ij})$ is the electron quadrupole operator, e is the electron's charge, $\hat{\boldsymbol{r}}_\alpha$ is the position of the α-th electron within the atom with summation over all electrons and the origin is chosen to be $\boldsymbol{R}$, the position of the nuclei within the atom. Dipole interaction induces the emission and absorption of radiation between the atomic ground S electron orbital state and the excited P orbital state, while quadrupole interaction induces the emission and absorption of radiation between the atomic ground S electron orbital state and the excited D orbital state as illustrated in Fig. 1. As the dipole and quadrupole transitions correspond to different selection rules, i.e., $\Delta l = \pm 1$ and $\Delta l = \pm 2$, we thus deal with the two transitions separately.

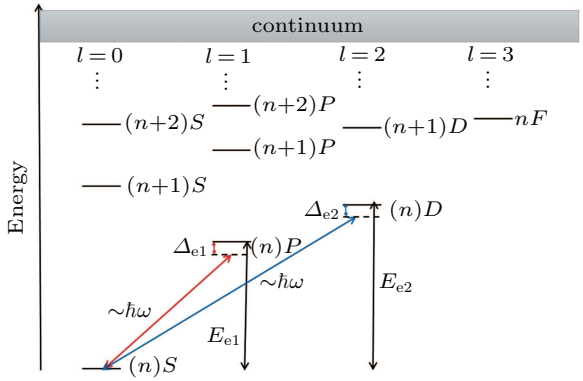


Fig. 1. (color online) Typical atomic energy level structure. Δ_{e1} and Δ_{e2} are the detuning of the electric dipole transition (red arrow) and the quadrupole transition (blue arrow), respectively. E_{e1} and E_{e2} are the energy of the excited P and D orbital states, respectively. $\hbar\omega$ is the energy of the optical field.

The atom is described by the Hamiltonian

$$\hat{H}_{\mathrm{at}} = E_{\mathrm{e}}\hat{P}_{\mathrm{e}} + \frac{\Delta_{\mathrm{FS}}}{\hbar^2}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}, \quad (7)$$

where Δ_{FS} is the fine-structure coupling constant, $\hat{P}_{\mathrm{g,e}}$ are the projectors onto the ground or excited state (the excited state represents the P state or D state of the dipole or quadrupole transition, respectively), and $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$ are the total electronic orbital and spin angular momentum, respectively. The hyperfine splitting Δ_{HFS} is not considered here since $E_{\mathrm{e}} \gg \Delta_{\mathrm{FS}} \gg \Delta_{\mathrm{HFS}}$ and the atom–light detuning $\Delta_{\mathrm{e}} \equiv E_{\mathrm{e}} - \hbar\omega$ from the excited state is generally much larger than Δ_{HFS}.

In the frame rotating with frequency ω via a unitary transformation $\hat{U}_{\mathrm{rot}}(t) = \mathrm{e}^{-\mathrm{i}\omega t\hat{P}_{\mathrm{e}}}$, the atomic Hamiltonian transforms as $\hat{H}_{\mathrm{at}} \to \hat{H}'_{\mathrm{at}} = \hat{H}_{\mathrm{at}} - \mathrm{i}\hbar\hat{U}^\dagger_{\mathrm{rot}}(t)\partial_t\hat{U}_{\mathrm{rot}}(t) = \Delta_{\mathrm{e}}\hat{P}_{\mathrm{e}} + (\Delta_{\mathrm{FS}}/\hbar^2)\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$, while the dipole Hamiltonian becomes

$$\begin{aligned}\hat{H}'_{\mathrm{d}} &= \hat{U}^\dagger_{\mathrm{rot}}(t)\hat{H}_{\mathrm{d}}\hat{U}_{\mathrm{rot}}(t) \\ &= -(\hat{P}_{\mathrm{g}} + \hat{P}_{\mathrm{e}}\mathrm{e}^{\mathrm{i}\omega t})\sum_j \hat{d}_j E_j \cos(\boldsymbol{k}\cdot\boldsymbol{R} + \phi_j - \omega t) \\ &\quad \times (\hat{P}_{\mathrm{g}} + \hat{P}_{\mathrm{e}}\mathrm{e}^{-\mathrm{i}\omega t}) \\ &\approx \sum_j\left(\frac{1}{2}\widetilde{E}_j\hat{P}_{\mathrm{e}}\hat{d}_j\hat{P}_{\mathrm{g}} + \frac{1}{2}\widetilde{E}^*_j\hat{P}_{\mathrm{g}}\hat{d}_j\hat{P}_{\mathrm{e}}\right), \end{aligned} \quad (8)$$

where we have introduced a complex field $\widetilde{E}_j = E_j\mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_j)}$ and applied the rotating-wave approximation (RWA) to drop terms oscillating at frequencies ω, 2ω, and higher ones in the last step of Eq. (8). When the energy of the optical field ($\sim\hbar\omega$) is far off-resonant with the transition energy E_{e},[19–24] the excited states can be eliminated adiabatically, and one can obtain the following effective Hamiltonian to the second order in perturbation theory[25]

$$(\hat{H}_{\mathrm{eff}})^{\mathrm{d}} = -\hat{P}_{\mathrm{g}}\hat{H}'_{\mathrm{d}}\hat{H}'^{-1}_{\mathrm{at}}\hat{H}'_{\mathrm{d}}\hat{P}_{\mathrm{g}}. \quad (9)$$

Dipole interaction is thoroughly discussed in Ref. [19]. In the regime of $\Delta_{\mathrm{FS}} \ll \Delta_{\mathrm{e1}}$ where Δ_{e1} is the detuning of the dipole transition, the effect of the fine-structure splitting can be

neglected. In $\Delta_{\rm FS}=0$ case, the explicit form of above Hamiltonian takes

$$(\hat{H}_{\rm eff})^{d} = -\frac{\hat{P}_{\rm g}\hat{\boldsymbol{d}}^2\hat{P}_{\rm g}}{12\Delta_{\rm e1}}|\widetilde{\boldsymbol{E}}|^2 = u_{\rm s}|\widetilde{\boldsymbol{E}}|^2\hat{P}_{\rm g} \tag{10}$$

with

$$u_{\rm s} = -\frac{|\langle l=0||\hat{\boldsymbol{d}}||l'=1\rangle|^2}{12\Delta_{\rm e1}}.$$

Here the relations $\hat{P}_{\rm e}\hat{P}_{\rm g}=0$, $\hat{P}_{\rm e}^2=\hat{P}_{\rm e}, \hat{P}_{\rm g}^2=\hat{P}_{\rm g}$, and $\hat{P}_{\rm e}+\hat{P}_{\rm g}=1$ are used. Equation (10) suggests that the dipole interaction yields a scalar light shift which is proportional to the square of the optical field strength $|\widetilde{\boldsymbol{E}}|^2$. The pre-factor is proportional to the transition matrix element $|\langle l=0||\hat{\boldsymbol{d}}||l'=1\rangle|^2 = \sum_{m'_L=0,\pm1}|\langle l=0,m_L=0|\hat{\boldsymbol{d}}|l'=1,m'_L\rangle|^2$.

When the effect of the fine-structure splitting is considered, the dipole interaction yields a vector light shift in addition to the scalar light shift of Eq. (10) as

$$(\hat{H}_{\rm eff})^{\rm d} = u_{\rm s}|\widetilde{\boldsymbol{E}}|^2\hat{P}_{\rm g} + \frac{\rm i}{\hbar}u_{\rm v}(\widetilde{\boldsymbol{E}}^*\times\widetilde{\boldsymbol{E}})\cdot\hat{\boldsymbol{S}}\hat{P}_{\rm g} \tag{11}$$

with

$$u_{\rm s} = -\frac{|\langle l=0||\hat{\boldsymbol{d}}||l'=1\rangle|^2}{36\Delta_{\rm e1}}\left(\frac{2}{1+\Delta_{\rm FS}/2\Delta_{\rm e1}}+\frac{1}{1-\Delta_{\rm FS}/\Delta_{\rm e1}}\right),$$
$$u_{\rm v} = \frac{\Delta_{\rm FS}/\Delta_{\rm e1}}{1-\Delta_{\rm FS}/2\Delta_{\rm e1}}u_{\rm s}.$$

Here the Levi–Civita symbol $\varepsilon_{iml}\varepsilon_{ljk} = \varepsilon_{lim}\varepsilon_{ljk} = \delta_{ij}\delta_{mk} - \delta_{ik}\delta_{mj}$ and the identity $\hat{S}_k\hat{S}_m = (\hbar^2/4)\delta_{km} + (i\hbar/2)\varepsilon_{kmn}\hat{S}_n$ are used. In the regime of $\Delta_{\rm FS}\ll\Delta_{\rm e}$, equation (11) recovers to Eq. (10).

Let us now turn to the quadrupole transition (see the blue arrow in Fig. 1.), similar treatment can be applied. After a tedious derivation (see Appendix A for detail), the quadrupole Hamiltonian in the rotating frame under RWA becomes

$$\begin{aligned}\hat{H}'_{\rm quad} &= \hat{U}^{\dagger}_{\rm rot}(t)\hat{H}_{\rm quad}\hat{U}_{\rm rot}(t)\\ &\approx \frac{\rm i}{12}\sum_i\sum_j(\hat{P}_{\rm e}\hat{Q}_{ij}\hat{P}_{\rm g}k_i\widetilde{E}_j - \hat{P}_{\rm g}\hat{Q}_{ij}\hat{P}_{\rm e}k_i\widetilde{E}^*_j).\end{aligned} \tag{12}$$

When we first consider no fine structure case with $\Delta_{\rm FS}=0$, the corresponding effective perturbation Hamiltonian gives

$$\begin{aligned}(\hat{H}_{\rm eff})^{\rm quad} &= -\hat{P}_{\rm g}\hat{H}'_{\rm quad}\hat{H}'^{-1}_{\rm at}\hat{H}'_{\rm quad}\hat{P}_{\rm g}\\ &= -\frac{\hat{P}_{\rm g}\hat{Q}_{ij}\hat{P}_{\rm e}\hat{Q}_{kl}\hat{P}_{\rm g}}{144\Delta_{\rm e2}}k_ik_k\widetilde{E}^*_j\widetilde{E}_l.\end{aligned} \tag{13}$$

From Eq. (13), we can see that the quadrupole interaction yields a light shift which is proportional to the optical field component E_j and the wave vector component k_j, with the pre-factor being proportional to the transition matrix element $\langle l=0||\hat{Q}_{ij}||l'=2\rangle$.

Let us then consider a finite fine-structure coupling. Using the relation $\hat{H}'^{-1}_{\rm at} = \hat{H}_0^{-1} - \hat{H}_0^{-1}\hat{V}\hat{H}'^{-1}_{\rm at}$ with $\hat{H}'_{\rm at} = \hat{H}_0+\hat{V} = \Delta_{\rm e}\hat{P}_{\rm e} + (\Delta_{\rm FS}/\hbar^2)\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$, the corresponding effective perturbation Hamiltonian gives

$$\begin{aligned}(\hat{H}_{\rm eff})^{\rm quad} &= -\hat{P}_{\rm g}\hat{H}'_{\rm quad}\left(\frac{\hat{P}_{\rm e}}{\Delta_{\rm e2}} - \frac{1}{\Delta_{\rm e2}}\frac{\Delta_{\rm FS}}{\hbar^2}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\hat{H}'^{-1}_{\rm at}\right)\hat{H}'_{\rm quad}\hat{P}_{\rm g}\\ &= -\frac{1}{144\Delta_{\rm e2}}\hat{P}_{\rm g}\hat{Q}_{ij}\hat{P}_{\rm e}\hat{Q}_{mn}\hat{P}_{\rm g}k_ik_m\widetilde{E}^*_j\widetilde{E}_n\\ &\quad+\frac{{\rm i}\Delta_{\rm FS}}{144\Delta_{\rm e2}\hbar}\hat{S}_k(\hat{P}_{\rm g}\hat{Q}_{il}\hat{P}_{\rm e}\hat{H}'^{-1}_{\rm at}\hat{P}_{\rm e}\hat{Q}_{mn}\hat{P}_{\rm g}\varepsilon_{jkl}\\ &\quad+\hat{P}_{\rm g}\hat{Q}_{lj}\hat{P}_{\rm e}\hat{H}'^{-1}_{\rm at}\hat{P}_{\rm e}\hat{Q}_{mn}\hat{P}_{\rm g}\varepsilon_{ikl})k_ik_m\widetilde{E}^*_j\widetilde{E}_n.\end{aligned} \tag{14}$$

For the $\Delta_{\rm FS}\ll\Delta_{\rm e2}$ situation, the effective perturbation Hamiltonian gives

$$\begin{aligned}(\hat{H}_{\rm eff})^{\rm quad} &\approx -\frac{(\hat{P}_{\rm g}\hat{Q}_{ij}\hat{P}_{\rm e}\hat{Q}_{mn}\hat{P}_{\rm g})}{144\Delta_{\rm e2}}k_ik_m\widetilde{E}^*_j\widetilde{E}_n\\ &\quad+\frac{\rm i}{\hbar}\frac{\Delta_{\rm FS}}{144\Delta^2_{\rm e2}}(\varepsilon_{jkl}\hat{P}_{\rm g}\hat{Q}_{il}\hat{P}_{\rm e}\hat{Q}_{mn}\hat{P}_{\rm g}\\ &\quad+\varepsilon_{ikl}\hat{P}_{\rm g}\hat{Q}_{lj}\hat{P}_{\rm e}\hat{Q}_{mn}\hat{P}_{\rm g})k_ik_m\widetilde{E}^*_j\widetilde{E}_n\hat{S}_k,\end{aligned} \tag{15}$$

where the first term is the scalar light shift term and the second term gives rise to a vector light shift.

3. Results and discussion

We now turn to investigate the effect of the dipole and quadrupole interaction on the ground state energy. It is shown that in Eqs. (11) and (15) that the vector light shift is about $\Delta_{\rm FS}/\Delta_{\rm e}$ times smaller than the scalar light shift for both dipole interaction and quadrupole interaction. To get a glance of the effects of dipole and quadrupole interaction, here we only compare the scalar light shifts due to electric dipole interaction and electric quadrupole interaction. From Eqs. (10) and (13), we can obtain the ground state energy shifts induced by the dipole and quadrupole transitions, which are given by

$$\delta_{\rm d} = \langle g|(\hat{H}_{\rm eff})^d|g\rangle = -\frac{e^2}{12\Delta_{\rm e1}}\eta_{\rm d}|\widetilde{\boldsymbol{E}}|^2 \tag{16}$$

$$\delta_{\rm quad} = \langle g|(\hat{H}_{\rm eff})^{\rm quad}|g\rangle = -\frac{e^2}{16\Delta_{\rm e2}}\eta_{\rm quad}k^2|\widetilde{\boldsymbol{E}}|^2. \tag{17}$$

Here without loss of generality, we have chosen a specific electric field $\widetilde{\boldsymbol{E}} = \widetilde{E}\cos(kx-\omega t)\boldsymbol{e}_y$ to show the energy corrections explicitly. $\eta_{\rm d} = \sum_{i=1,2,3}\sum_{m'_L=0,\pm1}|\langle l=0,m_L=0|\hat{r}_i|l'=1,m'_L\rangle|^2$ and $\eta_{\rm quad} = \sum_{m'_L=0,\pm1,\pm2}|\langle l=0,m_L=0|\hat{x}\hat{y}|l'=2,m'_L\rangle|^2$ are the transition matrixes of these two processes, respectively.

The energy corrections are then characterized by the ratio between two transitions, which is

$$\frac{\delta_{\rm quad}}{\delta_{\rm d}} = \frac{3\Delta_{\rm e1}}{4\Delta_{\rm e2}}k^2\eta \tag{18}$$

with $\eta = \eta_{\rm quad}/\eta_{\rm d}$. Apparently, it depends on the atom–light detunings $\Delta_{\rm e1}$, $\Delta_{\rm e2}$ of both transitions, the wave vector k of the light field, and the transition matrixes ratio η.

Now we do numerical comparisons for alkali atoms as examples to get a more intuitive understanding. It is reasonable to use hydrogen atom wave functions $\psi_{nlm}(r,\theta,\phi) = \mathrm{R}_{nl}(r)\mathrm{Y}_{lm}(\theta,\phi)$[4,25,26] to perform the integration. Here $\Delta_{e1} = \Delta_{e2} = \Delta_e$ are set to be 10^{10} Hz. The magnitude of electric wave vector $k = \omega/c$ and ω are obtained from the energy level $E_n = -Rhc/(n-\delta_l)^2$ where R is the Rydberg constant, h is Planck's constant, c is the speed of light, n is the principal quantum number, and δ_l is Rydberg's correction which describes an angular momentum-dependent quantum defect. Rydberg's correction δ_l is independent of n, but it is a function of the quantum number l and decreases rapidly with l. Here we consider only the ground state and use the data for δ_s from Refs. [4] and [26]. The dipole and quadrupole transition matrix elements, η_d and η_{quad}, and the ratio of two effects on ground state energy δ_{quad}/δ_d are listed in Table 1, η are illustrated in Fig. 2 and δ_{quad}/δ_d are illustrated in Fig. 3.

Table 1. Electric dipole and quadrupole impacts on the alkali atomic ground state manifold.

	Lithium	Sodium	Potassium	Rubidium	Caesium	Francium
Atom number	3	11	19	37	55	87
Electron configuration	$2S^1$	$3S^1$	$4S^1$	$5S^1$	$6S^1$	$7S^1$
δ_s	0.41	1.37	2.23	3.19	4.13	~ 5.10
$\eta_d(a_0^2)$	9.39	29.9	72.5	149.18	274.19	464.53
$\eta_{quad}(a_0^4)$	184.68	2591.71	17496.8	79834.8	283056	839901
Δ_e/Hz	10^{10}	10^{10}	10^{10}	10^{10}	10^{10}	10^{10}
ω/Hz	8.11×10^{14}	7.63×10^{14}	6.21×10^{14}	5.88×10^{14}	5.41×10^{14}	5.20×10^{14}
δ_{quad}/δ_d	3.02×10^{-7}	1.18×10^{-6}	2.18×10^{-6}	6.59×10^{-6}	1.54×10^{-5}	3.37×10^{-5}

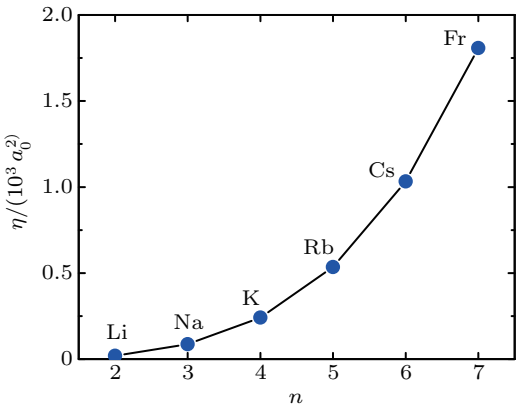


Fig. 2. (color online) The transition matrix element ration η in terms of principle quantum number n. η is in unit of a_0^2, where a_0 is the Bohr radius.

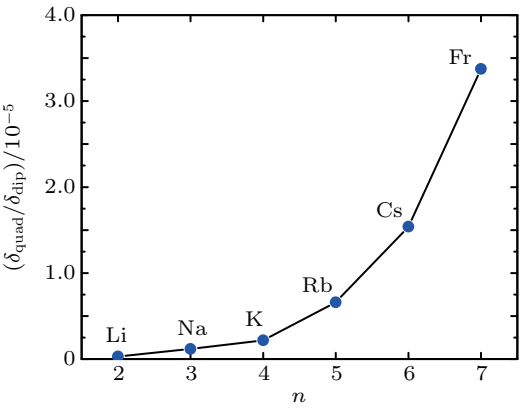


Fig. 3. (color online) The comparison of the impacts of the electric dipole and quadrupole coupling terms on the atomic ground state manifold to second order in perturbation theory, δ_{quad}/δ_d, in terms of principle quantum number n.

Figure 2 shows that the ratio η is increasing with the principle quantum number n which means η_{quad} is increasing much more rapidly than η_d. Figure 3. shows that for all alkali atoms the ground state energy shift by electric quadrupole interaction is about $10^{-7} \sim 10^{-5}$ times smaller than that by electric dipole interaction. This behavior can be understood from Eq. (18). Taking Bohr radius $a_0 = 0.53\times10^{-10}$ m and ω about 10^{14} Hz, $k^2a_0^2 = (\omega a_0/c)^2$ is then about 10^{-8} which makes the effect by electric quadrupole interaction much less than that by electric dipole interaction even the quadrupole transition element is $10^2 \sim 10^3$ times larger than the dipole transition matrix element in units of a_0^2. Physically, $ka_0 \ll 1$ means that the optical wave length is much larger than the size of the atom. And in this regime, the atom sees a spatially almost constant electric field and therefore the quadrupole effect which couples to the electric field gradient can be negligible, suggesting that the electric dipole approximation used in previous literature works well for alkali-like atoms.

Despite of the validity of the dipole approximation for alkali atoms, there may exist the situations where the quadrupole effect is considerable and one needs to go beyond the dipole approximation. First, we notice that, we have used a plane wave light field in above discussions, which naturally falls into the electric dipole approximation regime with $ka_0 \ll 1$. If we consider a short pulse laser with much larger electric field gradient, it may lead to a much larger electric quadrupole contribution. Second, for a Rydberg atom, which is an excited atom with one or more electrons that have a very high principal quantum number, it has a very large atom size which is comparable to the light field wave length. Under this condition, the electric quadrupole interaction might become important and cannot be ignored. Third, in this paper, we mainly consider the alkali-like atoms which have large electric dipole moments.

While for the molecule with a relative large quadrupole moment such as the carbon dioxide, the effect of the quadrupole interaction may become significant.

4. Summary

In this paper, we have studied the dipole and quadrupole coupling between an atom and a light field. In the far off-resonance case, we derive the effective Hamiltonians to describe the effects on the ground state manifold brought by the dipole and quadrupole transitions. We find that, for the alkali-like atoms, the energy correction from dipole transition is dominant and the dipole approximation can be applied. While for other cases like the Rydberg atom with a very large size, the molecular with large quadrupole moment, the correction induced by the quadrupole interaction may become considerable and one needs to go beyond the dipole approximation. Future studies would include Rydberg atoms, a gaussian-like light field, a many-electron atom, and so on.

Appendix A: Quadrupole interaction

In this section we focus on the next order light–atom coupling term — the electric quadrupole term — that gives the Hamiltonian

$$\hat{H}_{\rm quad} = -\frac{1}{6}\sum_i\sum_j \hat{Q}_{ij}\frac{\partial E_j(t)}{\partial r_i}(\boldsymbol{R}), \tag{A1}$$

where $\hat{Q}_{ij} = -e\sum_\alpha(3(\hat{r}_\alpha)_i(\hat{r}_\alpha)_j - \hat{r}_\alpha^2\delta_{ij})$ is the electron quadrupole operator, α sums over all electrons, e is the electron's charge, $\hat{r}_\alpha$ is the position of the α-th electron within the atom, and $\boldsymbol{R}$ is the position of the nuclei within the atom. For alkali atoms there is only one valance electron to be considered, therefore

$$\begin{aligned}\hat{Q}_{ij} &= -e(3\hat{r}_i\hat{r}_j - \hat{r}^2\delta_{ij})\\ &= -e\begin{bmatrix} 2\hat{x}^2-\hat{y}^2-\hat{z}^2 & 3\hat{x}\hat{y} & 3\hat{x}\hat{z}\\ 3\hat{y}\hat{x} & 2\hat{y}^2-\hat{x}^2-\hat{z}^2 & 3\hat{y}\hat{z}\\ 3\hat{z}\hat{x} & 3\hat{z}\hat{y} & 2\hat{z}^2-\hat{y}^2-\hat{x}^2\end{bmatrix}.\end{aligned} \tag{A2}$$

The electric quadrupole couples to the optical electric field gradient $E_j\cos(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_j)$

$$\nabla E = \begin{bmatrix} -E_xk_x\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_x) & -E_yk_x\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_y) & -E_zk_x\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_z)\\ -E_xk_y\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_x) & -E_yk_y\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_y) & -E_zk_y\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_z)\\ -E_xk_z\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_x) & -E_yk_z\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_y) & -E_zk_z\sin(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t+\phi_z)\end{bmatrix}. \tag{A3}$$

The electric quadrupole Hamiltonian term is therefore

$$\begin{aligned}\hat{H}_{\rm quad} = -\frac{e}{6}[&(2\hat{x}^2-\hat{y}^2-\hat{z}^2)k_xE_x\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t) + 3\hat{x}\hat{y}k_yE_x\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)\\ &+3\hat{x}\hat{z}k_zE_x\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)+3\hat{y}\hat{x}k_xE_y\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)\\ &+(2\hat{y}^2-\hat{x}^2-\hat{z}^2)k_yE_y\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)+3\hat{y}\hat{z}k_zE_y\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)\\ &+3\hat{z}\hat{x}k_xE_z\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)+3\hat{z}\hat{y}k_yE_z\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)\\ &+(2\hat{z}^2-\hat{x}^2-\hat{y}^2)k_zE_z\sin(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)].\end{aligned} \tag{A4}$$

Apply rotating wave approximation

$$\begin{aligned}\hat{H}'_{\rm quad} &= \hat{U}^\dagger_{\rm rot}(t)\hat{H}_{\rm quad}\hat{U}_{\rm rot}(t)\\ &= -\frac{e}{6}(\hat{P}_{\rm g}+\hat{P}_{\rm e}\,{\rm e}^{{\rm i}\omega t})\Bigg[(2\hat{x}^2-\hat{y}^2-\hat{z}^2)k_xE_x\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)}}{2{\rm i}}\\ &+3\hat{x}\hat{y}k_yE_x\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)}}{2{\rm i}}\\ &+3\hat{x}\hat{z}k_zE_x\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_x-\omega t)}}{2{\rm i}}+3\hat{y}\hat{x}k_xE_y\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)}}{2{\rm i}}\\ &+(2\hat{y}^2-\hat{x}^2-\hat{z}^2)k_yE_y\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)}}{2{\rm i}}+3\hat{y}\hat{z}k_zE_y\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_y-\omega t)}}{2{\rm i}}\\ &+3\hat{z}\hat{x}k_xE_z\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)}}{2{\rm i}}+3\hat{z}\hat{y}k_yE_z\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)}}{2{\rm i}}\\ &+(2\hat{z}^2-\hat{x}^2-\hat{y}^2)k_zE_z\frac{{\rm e}^{{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)}-{\rm e}^{-{\rm i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_z-\omega t)}}{2{\rm i}}\Bigg](\hat{P}_{\rm g}+\hat{P}_{\rm e}\,{\rm e}^{-{\rm i}\omega t})\end{aligned}$$

$$\approx -\frac{e}{12\mathrm{i}}\{\hat{P}_\mathrm{e}[(2\hat{x}^2-\hat{y}^2-\hat{z}^2)k_x\widetilde{E}_x+3\hat{x}\hat{y}k_y\widetilde{E}_x+3\hat{x}\hat{z}k_z\widetilde{E}_x+3\hat{y}\hat{x}k_x\widetilde{E}_y+(2\hat{y}^2-\hat{x}^2-\hat{z}^2)k_y\widetilde{E}_y$$
$$+3\hat{y}\hat{z}k_z\widetilde{E}_y+3\hat{z}\hat{x}k_x\widetilde{E}_z+3\hat{z}\hat{y}k_y\widetilde{E}_z+(2\hat{z}^2-\hat{x}^2-\hat{y}^2)k_z\widetilde{E}_z]\hat{P}_\mathrm{g}$$
$$-\hat{P}_\mathrm{g}[(2\hat{x}^2-\hat{y}^2-\hat{z}^2)k_x\widetilde{E}_x^*+3\hat{x}\hat{y}k_y\widetilde{E}_x^*+3\hat{x}\hat{z}k_z\widetilde{E}_x^*+3\hat{y}\hat{x}k_x\widetilde{E}_y^*+(2\hat{y}^2-\hat{x}^2-\hat{z}^2)k_y\widetilde{E}_y^*$$
$$+3\hat{y}\hat{z}k_z\widetilde{E}_y^*+3\hat{z}\hat{x}k_x\widetilde{E}_z^*+3\hat{z}\hat{y}k_y\widetilde{E}_z^*+(2\hat{z}^2-\hat{x}^2-\hat{y}^2)k_z\widetilde{E}_z^*]\hat{P}_\mathrm{e}\}, \tag{A5}$$

where $\widetilde{E}_i = E_i\,\mathrm{e}^{\mathrm{i}(\boldsymbol{k}\cdot\boldsymbol{R}+\phi_i)}$.

We study the impact of this coupling term on the atomic ground state manifold to second order in perturbation theory. We analyze the lowest energy electric quadrupole transition in an alkali atom, between the ground $(n)S$ electron orbital and the excited $(n)D$ orbital with excitation $E_\mathrm{e} = E_{\mathrm{e}2}$, as pictured in Fig. 1.

First we consider the special case with $\Delta_\mathrm{FS} = 0$, the effective Hamiltonian is given by

$$\begin{aligned}(\hat{H}_\mathrm{eff})^\mathrm{quad} &= -\hat{P}_\mathrm{g}\hat{H}'_\mathrm{quad}\hat{H}'^{-1}_\mathrm{at}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{g}\\ &= -\frac{\hat{P}_\mathrm{g}\hat{Q}_{ij}\hat{P}_\mathrm{e}\hat{Q}_{kl}\hat{P}_\mathrm{g}}{144\Delta_{\mathrm{e}2}}k_ik_k\widetilde{E}_j^*\widetilde{E}_l\\ &= -\frac{e^2}{144\Delta_{\mathrm{e}2}}\hat{P}_\mathrm{g}[(2\hat{x}^2-\hat{y}^2-\hat{z}^2)k_x\widetilde{E}_x^*\\ &\quad+3\hat{x}\hat{y}k_y\widetilde{E}_x^*+3\hat{x}\hat{z}k_z\widetilde{E}_x^*+3\hat{y}\hat{x}k_x\widetilde{E}_y^*\\ &\quad+(2\hat{y}^2-\hat{x}^2-\hat{z}^2)k_y\widetilde{E}_y^*+3\hat{y}\hat{z}k_z\widetilde{E}_y^*+3\hat{z}\hat{x}k_x\widetilde{E}_z^*\\ &\quad+3\hat{z}\hat{y}k_y\widetilde{E}_z^*+(2\hat{z}^2-\hat{x}^2-\hat{y}^2)k_z\widetilde{E}_z^*]\hat{P}_\mathrm{e}\\ &\quad\times[(2\hat{x}^2-\hat{y}^2-\hat{z}^2)k_x\widetilde{E}_x+3\hat{x}\hat{y}k_y\widetilde{E}_x\\ &\quad+3\hat{x}\hat{z}k_z\widetilde{E}_x+3\hat{y}\hat{x}k_x\widetilde{E}_y+(2\hat{y}^2-\hat{x}^2-\hat{z}^2)k_y\widetilde{E}_y\\ &\quad+3\hat{y}\hat{z}k_z\widetilde{E}_y+3\hat{z}\hat{x}k_x\widetilde{E}_z+3\hat{z}\hat{y}k_y\widetilde{E}_z\\ &\quad+(2\hat{z}^2-\hat{x}^2-\hat{y}^2)k_z\widetilde{E}_z]\hat{P}_\mathrm{g}\\ &= -\frac{\hat{P}_\mathrm{g}(e\hat{r}_i\hat{r}_j)\hat{P}_\mathrm{e}(e\hat{r}_k\hat{r}_l)\hat{P}_\mathrm{g}}{16\Delta_{\mathrm{e}2}}k_ik_k\widetilde{E}_j^*\widetilde{E}_l. \end{aligned}\tag{A6}$$

Without loss of generality we choose a particular electric field $\widetilde{\boldsymbol{E}} = \widetilde{E}\cos(kx-\omega t)\boldsymbol{e}_y$ and thus

$$(\hat{H}_\mathrm{eff})^\mathrm{quad} = -\frac{e^2}{16\Delta_{\mathrm{e}2}}\hat{P}_\mathrm{g}\hat{x}\hat{y}\hat{P}_\mathrm{e}\hat{x}\hat{y}\hat{P}_\mathrm{g}k^2\widetilde{E}^*\widetilde{E}. \tag{A7}$$

The ground state energy shift can be obtained from the effective hamiltonian as follows:

$$\begin{aligned}\delta_\mathrm{quad} &= \langle g|(\hat{H}_\mathrm{eff})^\mathrm{quad}|g\rangle\\ &= -\frac{e^2}{16\Delta_{\mathrm{e}2}}|\widetilde{\boldsymbol{E}}|^2k^2\langle g|(\hat{P}_\mathrm{g}\hat{x}\hat{y}\hat{P}_\mathrm{e}\hat{x}\hat{y}\hat{P}_\mathrm{g})\rangle\\ &= -\frac{e^2k^2}{16\Delta_{\mathrm{e}2}}|\widetilde{\boldsymbol{E}}|^2\sum_{m'_L=0,\pm1,\pm2}|\langle l=0,m_L=0|\hat{x}\hat{y}|l'=2,m'_L\rangle|^2\\ &= -\frac{e^2}{16\Delta_{\mathrm{e}2}}\eta_\mathrm{quad}k^2|\widetilde{\boldsymbol{E}}|^2, \end{aligned}\tag{A8}$$

where $|l,m_L\rangle$ is the atomic wave function and $\eta_\mathrm{quad} = \sum_{m'_L=0,\pm1,\pm2}|\langle l=0,m_L=0|\hat{x}\hat{y}|l'=2,m'_L\rangle|^2$ is the quadrupole transition matrix element.

Now let us consider the situation with finite $\boldsymbol{L}\cdot\boldsymbol{S}$ coupling. Using the relation $\hat{H}'^{-1}_\mathrm{at} = \hat{H}_0^{-1} - \hat{H}_0^{-1}\hat{V}\hat{H}'^{-1}_\mathrm{at}$ with $\hat{H}'_\mathrm{at} = \hat{H}_0+\hat{V} = \Delta_\mathrm{e}\hat{P}_\mathrm{e} + (\Delta_\mathrm{FS}/\hbar^2)\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}$, the corresponding effective perturbation Hamiltonian gives

$$\begin{aligned}(\hat{H}_\mathrm{eff})^\mathrm{quad} &= -\hat{P}_\mathrm{g}\hat{H}'_\mathrm{quad}\hat{H}'^{-1}_\mathrm{at}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{g}\\ &= -\hat{P}_\mathrm{g}\hat{H}'_\mathrm{quad}\Big(\frac{\hat{P}_\mathrm{e}}{\Delta_{\mathrm{e}2}}-\frac{1}{\Delta_{\mathrm{e}2}}\frac{\Delta_\mathrm{FS}}{\hbar^2}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\hat{H}'^{-1}_\mathrm{at}\Big)\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{g}\\ &= -\frac{1}{\Delta_{\mathrm{e}2}}\hat{P}_\mathrm{g}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{e}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{g}\\ &\quad+\frac{1}{\Delta_{\mathrm{e}2}}\frac{\Delta_\mathrm{FS}}{\hbar^2}\hat{P}_\mathrm{g}\hat{H}'_\mathrm{quad}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\hat{H}'^{-1}_\mathrm{at}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{g}. \end{aligned}\tag{A9}$$

With $\boldsymbol{k}\cdot\widetilde{\boldsymbol{E}} = 0$, the first term in Eq. (A9) gives

$$\begin{aligned}&-\frac{1}{\Delta_{\mathrm{e}2}}\hat{P}_\mathrm{g}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{e}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{g}\\ &= -\frac{e^2}{16\Delta_{\mathrm{e}2}}\hat{P}_\mathrm{g}\hat{r}_i\hat{r}_j\hat{P}_\mathrm{e}\hat{r}_m\hat{r}_n\hat{P}_\mathrm{g}k_ik_m\widetilde{E}_j^*\widetilde{E}_n. \end{aligned}\tag{A10}$$

Using the commutative relation $[\hat{L}_i,\hat{r}_j] = \mathrm{i}\hbar\varepsilon_{ijk}\hat{r}_k$, we have

$$\begin{aligned}[\hat{Q}_{ij},\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}] &= [-e(3\hat{r}_i\hat{r}_j-\hat{r}^2\delta_{ij}),\hat{L}_k\hat{S}_k]\\ &= -3\mathrm{i}e\hbar(\varepsilon_{jkl}\hat{r}_i\hat{r}_l\hat{S}_k+\varepsilon_{ikl}\hat{r}_l\hat{r}_j\hat{S}_k). \end{aligned}\tag{A11}$$

Noting that the ground state has $\hat{\boldsymbol{L}}\hat{P}_\mathrm{g} = 0$, the second term in Eq. (A9) gives

$$\begin{aligned}&\frac{1}{\Delta_{\mathrm{e}2}}\frac{\Delta_\mathrm{FS}}{\hbar^2}\hat{P}_\mathrm{g}\hat{H}'_\mathrm{quad}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\hat{H}'^{-1}_\mathrm{at}\hat{H}'_\mathrm{quad}\hat{P}_\mathrm{g}\\ &= \frac{\Delta_\mathrm{FS}}{144\Delta_{\mathrm{e}2}\hbar^2}\hat{P}_\mathrm{g}\hat{Q}_{ij}\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\hat{P}_\mathrm{e}\hat{H}'^{-1}_\mathrm{at}\hat{P}_\mathrm{e}\hat{Q}_{mn}\hat{P}_\mathrm{g}k_i\widetilde{E}_j^*k_m\widetilde{E}_n\\ &= \frac{\Delta_\mathrm{FS}}{144\Delta_{\mathrm{e}2}\hbar^2}\hat{P}_\mathrm{g}([\hat{Q}_{ij},\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}]+\hat{\boldsymbol{L}}\cdot\hat{\boldsymbol{S}}\hat{Q}_{ij})\\ &\quad\times\hat{P}_\mathrm{e}\hat{H}'^{-1}_\mathrm{at}\hat{P}_\mathrm{e}\hat{Q}_{mn}\hat{P}_\mathrm{g}k_ik_m\widetilde{E}_j^*\widetilde{E}_n\\ &= \frac{\Delta_\mathrm{FS}}{144\Delta_{\mathrm{e}2}\hbar^2}\hat{P}_\mathrm{g}(-3\mathrm{i}e\hbar)(\varepsilon_{jkl}\hat{r}_i\hat{r}_l\hat{S}_k+\varepsilon_{ikl}\hat{r}_l\hat{r}_j\hat{S}_k)\\ &\quad\times\hat{P}_\mathrm{e}\hat{H}'^{-1}_\mathrm{at}\hat{P}_\mathrm{e}(-e)(3\hat{r}_m\hat{r}_n-\hat{r}^2\delta_{mn})\hat{P}_\mathrm{g}k_ik_m\widetilde{E}_j^*\widetilde{E}_n\\ &= \frac{\mathrm{i}\Delta_\mathrm{FS}e^2}{16\Delta_{\mathrm{e}2}\hbar}\hat{P}_\mathrm{g}(\varepsilon_{jkl}\hat{r}_i\hat{r}_l\hat{S}_k+\varepsilon_{ikl}\hat{r}_l\hat{r}_j\hat{S}_k)\\ &\quad\times\hat{P}_\mathrm{e}\hat{H}'^{-1}_\mathrm{at}\hat{P}_\mathrm{e}\hat{r}_m\hat{r}_n\hat{P}_\mathrm{g}k_ik_m\widetilde{E}_j^*\widetilde{E}_n. \end{aligned}\tag{A12}$$

Therefore the whole effective hamiltonian is given by

$$\begin{aligned}(\hat{H}_\mathrm{eff})^\mathrm{quad} &= -\frac{e^2}{16\Delta_{\mathrm{e}2}}\hat{P}_\mathrm{g}\hat{r}_i\hat{r}_j\hat{P}_\mathrm{e}\hat{r}_m\hat{r}_n\hat{P}_\mathrm{g}k_ik_m\widetilde{E}_j^*\widetilde{E}_n\\ &\quad+\frac{\mathrm{i}\Delta_\mathrm{FS}e^2}{16\Delta_{\mathrm{e}2}\hbar}(\hat{S}_k\hat{P}_\mathrm{g}\hat{r}_i\hat{r}_l\hat{P}_\mathrm{e}\hat{H}'^{-1}_\mathrm{at}\hat{P}_\mathrm{e}\hat{r}_m\hat{r}_n\hat{P}_\mathrm{g}\varepsilon_{jkl}\\ &\quad+\hat{S}_k\hat{P}_\mathrm{g}\hat{r}_l\hat{r}_j\hat{P}_\mathrm{e}\hat{H}'^{-1}_\mathrm{at}\hat{P}_\mathrm{e}\hat{r}_m\hat{r}_n\hat{P}_\mathrm{g}\varepsilon_{ikl})k_ik_m\widetilde{E}_j^*\widetilde{E}_n \end{aligned}$$

$$\approx -\frac{e^2(\hat{P}_g\hat{r}_i\hat{r}_j\hat{P}_e\hat{r}_m\hat{r}_n\hat{P}_g)}{16\Delta_{e2}}k_ik_m\widetilde{E}_j^*\widetilde{E}_n$$
$$+\frac{\mathrm{i}}{\hbar}\frac{\Delta_{FS}e^2}{16\Delta_{e2}^2}(\varepsilon_{jkl}\hat{P}_g\hat{r}_i\hat{r}_l\hat{P}_e\hat{r}_m\hat{r}_n\hat{P}_g$$
$$+\varepsilon_{ikl}\hat{P}_g\hat{r}_l\hat{r}_j\hat{P}_e\hat{r}_m\hat{r}_n\hat{P}_g)k_ik_m\widetilde{E}_j^*\widetilde{E}_n\hat{S}_k, \qquad \text{(A13)}$$

where the approximation works for the $\Delta_{FS} \ll \Delta_{e2}$ situation. The first term in Eq. (A13) is the scalar shift term and the second term gives rise to a vector light shift.

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