

Multipole expansion for dispersion forces

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Light-matter interaction models invariably rely on the multipole expansion of the electromagnetic potentials generated by complex charge distributions. These multipoles are typically taken to be traceless; however, for a correct evaluation of dispersion forces at all distances, the validity of this assumption has to be checked carefully. Here, we revisit the concept of dispersion forces on an atom near a dielectric surface from the perspective of macroscopic quantum electrodynamics and find that, beyond the quadrupole, the multipoles cannot always be taken as fully traceless. In particular, we show that the trace of the octupole moment contributes to Casimir-Polder interactions beyond the electrostatic regime.

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Introduction. At the heart of any light-matter interaction lies the multipole expansion [1,2], by which the Coulomb interaction potential at some observation point $\mathbf{r}$ is expanded in a Taylor series about the source charge at $\mathbf{r}' = \mathbf{0}$. In free space, this results in

$$V(\mathbf{r} - \mathbf{r}') = \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{r} + r'_i \frac{\partial V}{\partial r'_i} \bigg|_{\mathbf{r}'=0} + \frac{r'_i r'_j}{2!} \frac{\partial^2 V}{\partial r'_i \partial r'_j} \bigg|_{\mathbf{r}'=0} + \frac{r'_i r'_j r'_k}{3!} \frac{\partial^3 V}{\partial r'_i \partial r'_j \partial r'_k} \bigg|_{\mathbf{r}'=0} \dots, \quad (1)$$

with the derivatives at $\mathbf{r}' = \mathbf{0}$ encoding the structure of each multipole moment. As the Coulomb potential satisfies the Laplace equation, the multipoles can be chosen to be traceless. For example, for the quadrupole moment one finds that

$$r'_i r'_j \frac{\partial^2 V}{\partial r'_i \partial r'_j} \bigg|_{\mathbf{r}'=0} = \left(r'_i r'_j - \frac{1}{3} \delta_{ij} r'^2 \right) \frac{\partial^2 V}{\partial r'_i \partial r'_j} \bigg|_{\mathbf{r}'=0}. \quad (2)$$

This condition is equivalent to decomposing the angular momentum into direct sums of multipoles $m_{i_1, i_2, \dots, i_\ell}$ of

order ℓ ,

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{\ell=0}^{\infty} m_{i_1, i_2, \dots, i_\ell} \frac{r'^\ell}{r^{\ell+1}} \times \sum_{m=-\ell}^{\ell} (-1)^m \sqrt{\frac{4\pi}{2\ell+1}} Y_{\ell m}(\theta, \phi) \quad (r' < r). \quad (3)$$

In the electrostatic regime, the traceless multipoles allow for a succinct and, in most situations, accurate calculation of a diverse array of physical interactions, ranging from the ubiquitous electric dipole-dipole interactions, which are the foundation for characterizing physical and chemical properties of atoms and molecules [1,3–5], to crystals in solid-state physics [6,7]. Once going outside the electrostatic regime, one has to question the validity of the traceless condition for the multipole moments. A pertinent example regards dispersion interactions between atoms and surfaces, i.e., the Casimir-Polder interaction [8] that, at least in the nonretarded limit, can be intuitively understood as the interaction of an atomic multipole with its surface-induced image, mediated by ground-state fluctuations of the quantized electromagnetic field. Up to now, the main focus in the field of dispersion forces had been mostly on electric dipole moments. With the advent of experimental techniques to probe highly excited Rydberg atoms near surfaces [9–12], it has become necessary to include also higher-order multipoles in order to precisely describe atom-surface interactions [13].

Recently, we have shown that higher-order multipole transitions will influence measurements of the Casimir-Polder interaction of Rydberg atoms in microfabricated vapor cells [14] using thin-cell transmission or reflection spectroscopy [15,16]. There, in vapor cells with submicrometer wall separation, the effects of quadrupole and octupole moments

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become larger than the expected measurement accuracy [14], thereby necessitating their inclusion in the modeling of the atom-surface interaction [17]. In Ref. [14], it was shown that thin-cell spectroscopy can already register significant deviations from the electric dipole-electric dipole energy shifts for cell thicknesses starting at around 200 nm, making it necessary to consider quadrupole-quadrupole effects, for which an expression was derived in the nonretarded limit. This leaves open the question of multipole interactions just beyond the nonretarded regime. It was noted that trace components from octupole interactions can also potentially contribute for distances comparable to (i.e., just beyond) the nonretarded regime, even if it is exactly zero in the electrostatic limit.

As early as the 1970s, there have been detailed theoretical analyses that question the implicit assumption of the traceless multipole moments [18–22], and the topic has remained active in one form or another to this day [23–25]. In Ref. [18], the inconsistency in the description of magnetic (and electric) multipole moments for molecules is discussed in detail. The condition of tracelessness imposed on electric multipole moments beyond and including the quadrupole is found to be insufficient to describe the interaction energies associated with multipole coupling to an external field, and a nontraceless approach for all multipole orders is presented. This approach is further extended to the retarded (far-field) regime for chiral molecules [20].

In this Letter, we show the influence of multipole moments on dispersion forces. We show that, outside the electrostatic regime, the assumption of fully traceless multipole moments is incorrect, and certain index contractions cannot be taken traceless. As a result, we discover a term, emerging from octupole-dipole interactions. This contribution scales with the atom-surface distance d as $1/d^6$ in the retarded limit, coinciding with the respective scaling for the quadrupole-quadrupole interaction. However, this term only exists outside the nonretarded limit, which implies an emergence of this contribution at intermediate distances.

This Letter is organized as follows. In section *Multipole dispersion interaction near a dielectric inter face*, we show that, even for the Casimir-Polder interaction between an atom and a dielectric half-space, the use of traceless multipole moments is still permitted, at least in the electrostatic (nonretarded) limit. In section *Trace contribution in the retarded limit*, we then show an explicit example for the appearance of trace contributions to the dipole-octupole Casimir-Polder interaction in the retarded limit. Concluding remarks are given in section *Conclusions*.

Multipole dispersion interaction near a dielectric interface. In the physics of dispersion forces, one considers the interaction of an atom or molecule with the medium-assisted quantized electromagnetic field, in which the dielectric medium adds boundary conditions on the electromagnetic field at its interface with free space. This is taken into account within the Green's function expansion of the electromagnetic fields that, besides the free-space Green's function $\mathbf{G}^{(0)}$, also contains contributions $\mathbf{G}^{(1)}$ from the scattering off the matter-vacuum interface [8,26]. The Casimir-Polder potential is then commonly derived using second-order perturbation theory using the interaction

Hamiltonian

$$\hat{H}_{\text{int}} = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}(\mathbf{r}_A) - \hat{\mathbf{Q}} \bullet [\nabla \otimes \hat{\mathbf{E}}(\mathbf{r}_A)] - \hat{\mathbf{O}} \bullet [\nabla \otimes \nabla \hat{\mathbf{E}}(\mathbf{r}_A)] \cdots, \quad (4)$$

where $\bullet$ denotes the Frobenius inner product, $\hat{\mathbf{d}}$, $\hat{\mathbf{Q}}$, and $\hat{\mathbf{O}}$ are the electric dipole, quadrupole, and octupole operators, respectively, and $\hat{\mathbf{r}}_A$ is the atomic position [13]. The interaction Hamiltonian represents an expansion into successively higher multipoles (dipoles, quadrupoles, octupoles, etc.), contracted with derivatives of the electric field at the position of the atom.

Expanding the operator of the electric field in terms of dyadic Green's functions [26,27], the Casimir-Polder potential associated with dipole-dipole interactions at zero temperature can be written as

$$U_{\text{dip}}(\mathbf{r}_A) = \frac{\hbar\mu_0}{2\pi} \int_0^\infty d\xi \xi^2 [\alpha_{dd}^{(2)}(i\xi) \bullet \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi)], \quad (5)$$

with the dipole polarizability $\alpha_{dd}^{(2)}(i\xi)$ and the scattering part $\mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi)$ of the Green's tensor evaluated at imaginary frequencies.

Similarly, for quadrupole-quadrupole interaction, one finds [13]

$$U_{\text{quad}}(\mathbf{r}_A) = \frac{\hbar\mu_0}{2\pi} \int_0^\infty d\xi \xi^2 [\alpha_{qq}^{(4)}(i\xi) \bullet \nabla \otimes \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi) \otimes \overleftarrow{\nabla}], \quad (6)$$

with the quadrupole polarizability

$$\alpha_{qq}^{(4)}(\omega) = \frac{1}{\hbar} \sum_{k \neq n} \left[\frac{\mathbf{Q}_{nk} \otimes \mathbf{Q}_{kn}}{\omega_{kn} + \omega} + \frac{\mathbf{Q}_{nk} \otimes \mathbf{Q}_{kn}}{\omega_{kn} - \omega} \right] \quad (7)$$

given in terms of the quadrupole transition moments $\mathbf{Q}_{nk} = \langle n | e(\hat{\mathbf{r}} \otimes \hat{\mathbf{r}}) / 2 | k \rangle$ and atomic transition frequencies ω_{kn} . Note that the Frobenius product here acts as a generalized trace. Other types of multipole interactions can be read off by straightforward generalization. The number l of gradient operators acting from the left/right on the Green's tensor corresponds to the order 2^{l+1} of the multipole involved in the interaction.

Similar to free space, the multipoles in the Casimir-Polder interaction inherit their traceless nature from the Green's function, in case of dispersion interactions specifically from the scattering part. Let us recall an important property of the scattering Green's tensor. The full Green's tensor $\mathbf{G} = \mathbf{G}^{(0)} + \mathbf{G}^{(1)}$ obeys the inhomogeneous Helmholtz equation in the space including the dielectric material, whereas the free-space Green's tensor $\mathbf{G}^{(0)}$ obeys the inhomogeneous Helmholtz equation in free space. This means that the scattering part $\mathbf{G}^{(1)}$ satisfies a homogeneous Helmholtz equation as it relates to a source-free problem and is hence (double-sided) transverse, i.e., $\partial_i G_{ij}^{(1)} = G_{ij}^{(1)} \overleftarrow{\partial_j} = 0$.

This in turn means that any quadrupole-type interaction can be written using traceless quadrupole moments. To see this, let us decompose the quadrupole tensor Q_{ij} into a traceless part $\tilde{Q}_{ij}$ and its trace,

$$Q_{ij} = \tilde{Q}_{ij} + \frac{1}{3} \text{Tr}(\mathbf{Q}) \delta_{ij}. \quad (8)$$

Hence, the contraction of the quadrupole moment with the gradient of the Green's tensor, writing out the Frobenius product, is

$$Q_{ij}\partial_i G_{jk}^{(1)} = \tilde{Q}_{ij}\partial_i G_{jk}^{(1)} + \frac{1}{3}\text{Tr}(\mathbf{Q})\partial_i G_{ik}^{(1)} = \tilde{Q}_{ij}\partial_i G_{jk}^{(1)} \quad (9)$$

because the scattering Green's tensor is divergence-free. Hence, all dispersion interactions involving quadrupole moments can always be written using traceless quadrupole tensors, usually defined by [18]

$$\Theta_{ij} = \frac{1}{2}(3Q_{ij} - \text{Tr}\mathbf{Q}\delta_{ij}) = \frac{3}{2}\tilde{Q}_{ij}. \quad (10)$$

Let us turn to the octupole moments, defined in their traceless form as [18]

$$\Omega_{ijk} = \frac{1}{2}(5O_{ijk} - O_{ill}\delta_{jk} - O_{jll}\delta_{ik} - O_{kll}\delta_{ij}), \quad (11)$$

which are traceless in all pairs of tensor indices. Its contraction with suitably chosen gradients of the scattering Green's tensor then reads as

$$\begin{aligned} \Omega_{ijk}\partial_i\partial_j G_{km}^{(1)} &= \frac{5}{2}O_{ijk}\partial_i\partial_j G_{km}^{(1)} - \frac{1}{2}O_{ill}\partial_i\partial_j G_{jm}^{(1)} \\ &\quad - \frac{1}{2}O_{jll}\partial_i\partial_j G_{im}^{(1)} - \frac{1}{2}O_{kll}\partial_i\partial_j G_{km}^{(1)}. \end{aligned} \quad (12)$$

The second and third terms on the right-hand side of Eq. (12) again vanish due to the transverse nature of the scattering Green's tensor. However, the last term requires special attention. Recalling that $\mathbf{G}^{(1)}$ satisfies the homogeneous Helmholtz equation and is itself transverse, i.e., divergence-free, it satisfies

$$\Delta\mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}', \omega) + \frac{\omega^2}{c^2}\varepsilon(\mathbf{r}, \omega)\mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}', \omega) = \mathbf{0}. \quad (13)$$

This means that the scattering part of the Green's tensor does not fulfill the Laplace equation as does the static Coulomb potential [Eq. (1)]. Hence, the combination $\partial_i\partial_j G_{km}^{(1)}$ in Eq. (12) by itself does not immediately vanish, but it equates to $-k^2 G_{km}^{(1)}$.

Nevertheless, if we consider the electrostatic limit, where one defines the static Green's tensor as

$$\mathbf{\Gamma}(\mathbf{r}, \mathbf{r}') = \lim_{\omega \rightarrow 0} \frac{\omega^2}{c^2} \mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r}', \omega), \quad (14)$$

one indeed finds again that

$$\Omega_{ijk}\partial_i\partial_j\Gamma_{km} = \frac{5}{2}O_{ijk}\partial_i\partial_j\Gamma_{km}. \quad (15)$$

This means that in the nonretarded, electrostatic limit, all octupole (and higher-order) moments can be chosen again to be traceless.

However, in the general case, i.e., outside the limit of the electrostatic approximation, there is no immediate reason why the multipole moments beyond the quadrupole have to be traceless. This important conclusion applies to ongoing experiments in which Casimir-Polder interactions are investigated at intermediate distances, and in which higher-order multipole interactions are important. This requires precision experiments, typically involving not too highly excited Rydberg atoms, at submillimeter distances from a surface. The Rydberg excitations ensure that the extent of the electronic wave function is no longer negligible, so that field gradients near the surface become important, and hence higher-order multipole interactions become relevant. This has

to be balanced by the fact that the nonretarded regime extends further for larger principal quantum numbers n , as the dominant transitions have wavelengths that increase as n^3 . Therefore, we can surmise that low-lying Rydberg atoms are a good choice to see these effects, which point toward current experiments in nanocells [14]. Additionally, higher-order corrections could eventually also become of importance for metrological high-precision measurements of Casimir-Polder or Casimir interactions looking for forces [28].

Trace contribution in the retarded limit. As shown above, the contraction of the (traceful) octupole moment tensor O_{ijk} with the derivatives of the Green's tensor gives

$$O_{ijk}\partial_i\partial_j G_{km}^{(1)} = \frac{2}{5}\Omega_{ijk}\partial_i\partial_j G_{km}^{(1)} - \frac{\omega^2}{5c^2}O_{kll}G_{km}^{(1)}, \quad (16)$$

where, in the last term resulting from the trace of the octupole moment, we replaced the wave number $k \mapsto \omega/c$. Note that this has the appearance of an effective dipole moment, which can be seen as follows. Take, for example, the zzz component of the octupole tensor $e(\mathbf{r} \otimes \mathbf{r} \otimes \mathbf{r})/6$; its decomposition into spherical harmonics yields

$$\begin{aligned} \frac{e}{6}(\mathbf{r} \otimes \mathbf{r} \otimes \mathbf{r})_{zzz} &= \frac{e}{6}r^3 \cos^3 \Theta \\ &= \frac{e}{6}r^3 \left[\frac{4}{5}\sqrt{\frac{\pi}{7}}Y_{3,0}(\Theta, \varphi) + \frac{6}{5}\sqrt{\frac{\pi}{3}}Y_{1,0}(\Theta, \varphi) \right], \end{aligned} \quad (17)$$

which contains, besides the expected octupole term (with $l = 3$ in the spherical harmonic Y_{lm}), an effective dipole term (with $l = 1$) that derives solely from the trace of the octupole moment.

Because of the spherical harmonic Y_{lm} , the selection rules are identical to those of a dipole, $\Delta l = \pm 1$.

In second-order perturbation theory [8], the trace contribution to the energy shift is thus (see the Supplemental Material [29])

$$\begin{aligned} U_{od}^{\text{trace}}(\mathbf{r}_A) &= \frac{\mu_0}{5\hbar c^2} \sum_k \int_0^\infty \frac{d\omega}{\omega_k + \omega} \omega^4 \\ &\quad \mathbf{T}_{0k} \cdot \text{Im}\mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, \omega) \cdot \mathbf{d}_{k0}, \end{aligned} \quad (18)$$

where we have denoted $(\mathbf{T}_{0k})_i \equiv \langle 0 | \hat{O}_{il} | k \rangle$ for the transition $0 \rightarrow k$. This results in a contribution to the Casimir-Polder shift as

$$U_{od}^{\text{trace}}(\mathbf{r}_A) = \frac{\hbar\mu_0}{10\pi c^2} \int_0^\infty d\xi \xi^4 \text{Tr}[\boldsymbol{\alpha}_{od}^{(4)}(i\xi) \cdot \mathbf{G}^{(1)}(\mathbf{r}_A, \mathbf{r}_A, i\xi)]. \quad (19)$$

Note that the replacement $\omega \mapsto i\xi$ leads, via the extra two powers of ω , to a sign change. We have further defined an octupole-dipole polarizability

$$\boldsymbol{\alpha}_{od}^{(4)}(i\xi) = \frac{1}{\hbar} \sum_k \left(\frac{\mathbf{d}_{k0} \otimes \mathbf{T}_{0k}}{i\xi + \omega_k} - \frac{\mathbf{T}_{0k} \otimes \mathbf{d}_{k0}}{i\xi - \omega_k} \right), \quad (20)$$

with the effective dipole moment resulting from the octupole trace. Similarly, a dipole-octupole interaction can be derived in the same way with an analogous dipole-octupole polarizability (see the Supplemental Material [29]).

Let us now consider an atom near a planar interface and recall how the scattering Green's function for a half-space with the interface at $z = 0$ can be conveniently written, and how the retarded limit of the Casimir-Polder interaction can be subsequently derived.

Using the Fresnel reflection coefficients, the scattering Green's tensor in the coincidence limit is given by [8,26]

$$\begin{aligned} G^{(1)}(\mathbf{r}, \mathbf{r}, \omega) = & \frac{i}{8\pi} \int_0^\infty dq \frac{q}{\beta_0} e^{2i\beta_0 z_A} \\ & \times \left[r_s \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right. \\ & \left. + r_p \frac{c^2}{\omega^2} \begin{pmatrix} -\beta_0^2 & 0 & 0 \\ 0 & -\beta_0^2 & 0 \\ 0 & 0 & 2q^2 \end{pmatrix} \right], \quad (21) \end{aligned}$$

where $\beta_0 = \sqrt{\omega^2/c^2 - q^2}$ [$\text{Im}\beta_0 \geq 0$] is the z component of the wave number in free space and q is the component perpendicular to it.

Rotating to the imaginary frequency axis and defining $b_0 = \sqrt{\xi^2/c^2 + q^2}$, one finds the scattering Green's tensor at imaginary frequencies as [8]

$$\begin{aligned} G^{(1)}(\mathbf{r}, \mathbf{r}, i\xi) = & \frac{1}{8\pi} \int_{\xi/c}^\infty db_0 e^{-2b_0 z_A} \\ & \times \left[r_s \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right. \\ & \left. - r_p \frac{c^2}{\xi^2} \begin{pmatrix} b_0^2 & 0 & 0 \\ 0 & b_0^2 & 0 \\ 0 & 0 & 2b_0^2 - 2\frac{\xi^2}{c^2} \end{pmatrix} \right]. \quad (22) \end{aligned}$$

In the retarded limit, one assumes that the atom-surface distance z_A dominates over all transition wavelengths.

One can therefore approximate the atomic polarizability as well as the optical properties of the half-space by their static values, i.e., $\alpha_{od}^{(4)}(i\xi) \simeq \alpha_{od}(0)$ and $\varepsilon(i\xi) \simeq \varepsilon(0) \equiv \varepsilon$ [8,26].

Changing variables to $v = b_0 c / \xi$, the order of integration in the Casimir-Polder potential can be changed to

$$\int_0^\infty d\xi \int_{\xi/c}^\infty db_0 \mapsto \int_1^\infty dv \int_0^\infty d\xi \frac{\xi}{c}, \quad (23)$$

and integrating over ξ yields

$$\int_0^\infty d\xi \xi^5 e^{-2\xi v z_A / c} = \frac{15}{8} \left(\frac{c}{v z_A} \right)^6. \quad (24)$$

Combining everything yields the contribution of the octupole trace to the octupole-dipole Casimir-Polder energy in the

retarded limit as

$$\begin{aligned} U_{od}^{\text{trace}}(z_A) \simeq & \frac{3\hbar c}{128\pi^2 \varepsilon_0 z_A^6} \int_1^\infty \frac{dv}{v^6} \\ & \times \text{Tr} \left[\alpha_{od}(0) \cdot \left\{ r_s \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \right. \right. \\ & \left. \left. - r_p \begin{pmatrix} v^2 & 0 & 0 \\ 0 & v^2 & 0 \\ 0 & 0 & 2v^2 - 2 \end{pmatrix} \right\} \right], \quad (25) \end{aligned}$$

where the Fresnel reflection coefficients are approximated by

$$r_s \simeq \frac{v - \sqrt{\varepsilon - 1 + v^2}}{v + \sqrt{\varepsilon - 1 + v^2}}, \quad r_p \simeq \frac{\varepsilon v - \sqrt{\varepsilon - 1 + v^2}}{\varepsilon v + \sqrt{\varepsilon - 1 + v^2}}. \quad (26)$$

In the limit of a perfectly reflecting half-space with $r_s = -1$ and $r_p = 1$, one can even perform the v -integral to obtain

$$U_{od}^{\text{trace}}(z_A) \simeq -\frac{\hbar c}{160\pi^2 \varepsilon_0 z_A^6} \text{Tr} \left[\alpha_{od}(0) \cdot \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right]. \quad (27)$$

As expected, on dimensional grounds, the potential falls off as z_A^{-6} , despite the fact that the trace part of the octupole moment behaves as an effective dipole. This is the main result of this Letter that demonstrates a nonzero dipole-octupole contribution to the Casimir-Polder interaction in the retarded regime.

We now compare the trace contribution to the quadrupole-quadrupole interaction in order to estimate its potential impact. For that, we return to Eq. (6) and compute the quadrupole-quadrupole interaction in the retarded limit and perform a rotational averaging. Details of this calculation are given in Sec. II of the Supplemental Material [29]. The result is

$$U_{qq}(z_A) \simeq -\frac{5\hbar c}{64\pi^2 \varepsilon_0 z_A^6} \alpha_{qq}(0), \quad (28)$$

with the static, isotropic quadrupole polarizability $\alpha_{qq}(0)$. Performing a similar isotropic averaging to Eq. (6), we find for the ratio between the dipole-octupole trace and the quadrupole-quadrupole interaction in the retarded limit the simple result

$$\frac{U_{od} + U_{do}}{U_{qq}} = \frac{2}{15} \frac{\alpha_{od}(0) + \alpha_{do}(0)}{\alpha_{qq}(0)}, \quad (29)$$

showing that the trace part of the dipole-octupole interaction could be on the same order of magnitude as the quadrupole-quadrupole interaction. Indeed, taking the example of the $|6S_{1/2}\rangle$ ground state of cesium, the dipole-octupole energy shift amounts to approximately half the quadrupole-quadrupole shift (further details in the Supplemental Material [29]).

We also note here that while the magnetic dipole and the electric quadrupole interaction arise at the same level of perturbation theory, for atomic multipole interactions one has to also take into account how the relevant multipole transition moments scale with atomic properties. Electric multipole transition moments scale strongly with the principal quantum n ,

for example, dipole moments $d \propto n^2$, or quadrupole moments $q \propto n^4$, and so on. In contrast, magnetic transition moments are (almost) independent of the principal quantum number, as the magnetic moment operator $\hat{\mathbf{L}} + 2\hat{\mathbf{S}}$ does not affect the radial part of the atomic wave function. Thus, for the Rydberg atoms envisaged in our manuscript, electric multipole transitions will dominate over possible magnetic dipole transitions.

Conclusions. We have reconsidered the pertinent question of using traceless multipole moments in the computation of higher-order multipole dispersion forces. We have shown that the atomic multipole moments can still be chosen to be traceless in the nonretarded (or electrostatic) limit. This is due to the fact that the scattering part of the Green's tensor, which is responsible for the dispersion interaction, is transverse and, in the electrostatic limit, also obeys the

Laplace equation, which is crucial for the appearance of the traceless moments.

However, we also demonstrate that outside the nonretarded limit, where the scattering part of the Green's tensor merely solves the homogeneous Helmholtz equation, not all index pairs of the octupole tensor give a traceless contribution. We furthermore explicitly calculate this trace contribution in the retarded limit. Finally, we have outlined some possible experimental scenarios such as precision spectroscopy of Rydberg atoms confined in thin vapor cells or high-precision fundamental physics measurements and metrology, where the higher-order corrections discussed here could become relevant.

Data availability. No data were created or analyzed in this study.

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- [29] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/1q4p-stl6> for details on the calculation of the quadrupole-quadrupole interaction in the retarded limit.