Fluorescence profile of an NV centre in a nanodiamond

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Abstract

Nanodiamonds containing luminescent point defects are widely explored for applications in quantum bio-sensing such as nanoscale magnetometry, thermometry, and electrometry. A key challenge in the development of such applications is a large variation in fluorescence properties observed between particles, even when obtained from the same batch or nominally identical fabrication processes. By theoretically modelling the emission of nitrogen-vacancy colour centres in spherical nanoparticles, we are able to show that the fluorescence spectrum varies with the exact position of the emitter within the nanoparticle, with noticeable effects seen when the diamond radius, $a$, is larger than around 110 nm, and significantly modified fluorescence profiles found for larger particles when $a = 200$ nm and $a = 300$ nm, while negligible effects below $a = 100$ nm. These results show that the reproducible geometry of point defect position within narrowly sized batch of diamond crystals is necessary for controlling the emission properties. Our results are useful for understanding the extent to which nanodiamonds can be optimised for bio-sensing applications.

I. INTRODUCTION

Understanding nanoscale effects is one of the most exciting scientific endeavours. It underpins very diverse research areas such as the mechanisms of life [1–4], quantum information [5–7], and fundamental phenomena in condensed matter systems [8–10]. Research in these areas requires nanoscale quantum sensors, and one of the most mature room-temperature quantum nanoscale sensor is nanodiamond containing the negatively-charged nitrogen-vacancy (NV) centre [11, 12]. Such doped nanodiamonds are a superb system for quantum sensing. They are highly biocompatible [13, 14] and photostable [15, 16], and therefore are ideal for minimally invasive biological experiments.

In NV, readout is typically achieved via optically detected magnetic resonance (ODMR), where the resonances in the interaction of the electronic spin of NV centres and a radio frequency (RF) electromagnetic field are detected by measuring the photo luminescence intensity of the centres. In this way, NV centres have been used for nanoscale magnetometry [17, 18], electrometry [19, 20], thermometry [21, 22] and pressure measurements [23].

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Alternatively, accurate measurements of the photon luminescence spectrum (in particular its zero-phonon line) allows for all optical measurements [24].

A drawback of fluorescent nanodiamonds in comparison to quantum dots and organic molecules is their intrinsic heterogeneity. Large variations in fluorescence intensities and lifetimes are observed between NV centres in similar nanodiamonds [25–28]. Understanding the origins of such variations and the ways of reducing the heterogeneity is important for developing a reliable technological platform.

Here we show large variations in NV fluorescence by performing theoretical modelling of the fluorescence of of a point defect in spherical nanodiamonds as a function of nanodiamond size and the defect position within the crystal. To explore the effect of geometry on emission, we treat the NV phonon structure by a set of electric dipoles with fixed energy spacing and emission probabilities [29, 30], and the electromagnetic fields within and outside the diamond are calculated via Mie theory [31–34] which were also validated by the numerical solver [35]. In our calculations, the density of state modification for centres close to crystal surface [36] is not considered. Our results show that noticeable variations in the spectra and intensities appear when the particle radius, \( a \), is greater than around 110 nm, and the shapes of the spectra are significantly modified for larger crystals as shown for the cases at \( a = 200 \text{ nm} \) and \( a = 300 \text{ nm} \). The effect is negligible for sizes below \( a = 100 \text{ nm} \). Although our systems are idealised for computational tractability, our results highlight the sensitivity of fluorescence to the precise geometry of the NV-diamond system, and are therefore important for understanding the experimentally observed variations in fluorescence.

II. MODEL

To investigate how the NV centre location within a nanodiamond particle affects the far field fluorescence, we consider a single NV in a spherical particle with a refractive index of 2.4. The broad NV emission spectrum is represented by emission by 12 point dipoles \( p \equiv p_i \ (i = 0, 1, 2..., 11) \) corresponding to the NV de-exciting via a single photon and multiple phonons. This gives rise to a broad emission spectrum with components at different wavelengths, as listed in Table 1. We use the low temperature emission probabilities from Ref. [29, 30] as the relative intensity, \( R \), emitted from the NV centre at different numbers of de-exciting phonons, but we expect similar results for the room temperature case. Since
TABLE I. Probabilities (Relative intensity $R$) to emit photons and phonons of a NV centre in bulk diamond as a function of the number of phonons at low temperature calculated in Refs. [29]. The zero phonon line is indicated by ZPL, and the phononic sideband arises from the summation from 1 to 11 phonons.

| No. of phonons | Wavelength $\lambda$ (nm) | Emission probabilities (Relative intensity $R$) | Dipole moment strength (arb. u.) $(|p| = \lambda^2 \sqrt{R})$ |
|----------------|---------------------------|-----------------------------------------------|-------------------------------------------------|
| 0 (ZPL)       | 637                       | 0.0270                                        | 66674.65                                       |
| 1              | 659                       | 0.0951                                        | 133924.83                                      |
| 2              | 683                       | 0.173                                         | 194028.02                                      |
| 3              | 708                       | 0.209                                         | 229160.45                                      |
| 4              | 736                       | 0.191                                         | 236740.36                                      |
| 5              | 765                       | 0.140                                         | 218971.14                                      |
| 6              | 797                       | 0.0856                                        | 185846.13                                      |
| 7              | 832                       | 0.0441                                        | 145367.04                                      |
| 8              | 870                       | 0.0211                                        | 109946.08                                      |
| 9              | 912                       | 0.00931                                       | 80253.60                                       |
| 10             | 957                       | 0.00343                                       | 53637.80                                       |
| 11             | 1008                      | 0.000980                                      | 31807.83                                       |

Intensity $R$ is proportional to the field power, it is then proportional to the square of the strength of the represented electric dipole for the NV centre. To match the dimension, we have $(c|p|^2)/(4\pi\epsilon_0\epsilon_r\lambda^4) \sim R$ where $c$ is the speed of light, $\epsilon_0$ is the vacuum permittivity, $\epsilon_r$ is the relative permittivity and $\lambda$ is the wavelength of emission light. Since $c$, $\epsilon_0$ and $\epsilon_r$ are constant in a homogeneous diamond, for simplicity, we set $|p|^2 = \lambda^4 R$. In Fig. 3 (c-d), the square symbols display the relative intensity $R$ at the corresponding wavelengths.

To monitor the emission, we model a detector with pin hole and circular entrance aperture. The axis of the point dipole is assumed either parallel or perpendicular to the plane of the aperture, as sketched in Fig. 1.

All electric dipoles are co-located at $\mathbf{x}_d$ but each of them oscillates at a specific angular frequency $\omega \equiv \omega_i (i = 0, 1, 2..., 11)$ as $\exp(-i\omega t)$. The emitted electric and magnetic fields
from such a dipole are, respectively,

\[
E^d = \frac{1}{4\pi \epsilon_0 \epsilon_2} \frac{\exp(ik_2 r_d)}{r_d^3} \left\{ \left( -k_2^2 r_d^2 - 3ik_2 r_d + 3 \right) \frac{r_d \cdot \mathbf{p}}{r_d^2} r_d + \left( k_2^2 r_d^2 + ik_2 r_d - 1 \right) \mathbf{p} \right\}, \tag{1a}
\]

\[
H^d = \frac{\omega k_2}{4\pi} [r_d \times \mathbf{p}] \left( \frac{1}{r_d} - \frac{1}{ik_2 r_d^2} \right) \frac{\exp(ik_2 r_d)}{r_d} \tag{1b}
\]

where \( r_d = x - x_d \) with \( x \) being the field location of interest and \( r_d = |r_d| \), \( k_2 \) is the wavenumber, \( \epsilon_0 \) is the permittivity in vacuum, and \( \epsilon_2 = n_2^2 \) is the relative permittivity of diamond with \( n_2 = 2.4 \) the refractive index of diamond.

In a homogeneous medium, the intensity of each wavelength would be proportional to the photon emission probability in the actual spectrum at the same wavelength, which in turn is derived from the emission probabilities. However, the electromagnetic fields transmitted to the surrounding medium (air in this work) are modified due to the boundary conditions on the surface of the particle and can be obtained by solving Maxwell’s equations. In the frequency domain, the Maxwell’s equations in the internal domain of the nanodiamond and
the external domain are
\[ \nabla \times \mathbf{E}^j = i\omega\mu_0\mu_j\mathbf{H}^j, \quad (2a) \]
\[ \nabla \cdot \mathbf{E}^j = 0; \quad (2b) \]
\[ \nabla \times \mathbf{H}^j = -i\omega\epsilon_0\epsilon_j\mathbf{E}^j, \quad (2c) \]
\[ \nabla \cdot \mathbf{H}^j = 0 \quad (2d) \]
where \( \mu_0 \) is the permeability in vacuum, \( j \) refers to the external domain and the nanodiamond domain with \( j = 1 \) and \( j = 2 \), respectively, and \( \mu_j \) is the relative permeability of each domain which is set as \( \mu_1 = \mu_2 = 1 \) in this work.

Together with the boundary conditions,
\[ \mathbf{t}_1 \cdot (\mathbf{E}^2 + \mathbf{E}^d) = \mathbf{t}_1 \cdot \mathbf{E}^1, \quad \mathbf{t}_2 \cdot (\mathbf{E}^2 + \mathbf{E}^d) = \mathbf{t}_2 \cdot \mathbf{E}^1; \quad (3a) \]
\[ \mathbf{t}_1 \cdot (\mathbf{H}^2 + \mathbf{H}^d) = \mathbf{t}_1 \cdot \mathbf{H}^1, \quad \mathbf{t}_2 \cdot (\mathbf{H}^2 + \mathbf{H}^d) = \mathbf{t}_2 \cdot \mathbf{H}^1 \quad (3b) \]
where \( \mathbf{t}_1 \) and \( \mathbf{t}_2 \) are the two independent unit tangential directions on the diamond surface, the Maxwell’s equations \((2)\) are solved using the Mie theory, which is detailed in the Appendix \[A\]. After obtaining the electromagnetic fields, we can calculate the observed far-field intensity for each dipole as measured through the aperture located either at the top view position \((T)\) or the side view position \((S)\). This is done by integrating the time-averaged Poynting vector over the aperture area.

**Top view:**
\[ I_T(\lambda_i) = \int_{S_{obj}} \frac{1}{2} \left[ \mathbf{E}^i \times (\mathbf{H}^1)^* \right] \cdot \mathbf{e}_z \, dS, \quad i = 0, 1, 2, ..., 11; \quad (4a) \]

**Side view:**
\[ I_S(\lambda_i) = \int_{S_{obj}} \frac{1}{2} \left[ \mathbf{E}^i \times (\mathbf{H}^1)^* \right] \cdot \mathbf{e}_x \, dS, \quad i = 0, 1, 2, ..., 11. \quad (4b) \]

The above formulations can give us the overall photon counts with respect to the relative intensities of a NV centre in bulk diamond listed in Table \[I\] in which \( \lambda_i \) is the wavelength of the corresponding dipole, \( \mathbf{e}_x \) and \( \mathbf{e}_z \) are the unit vector along \( x \) and \( z \) axis, respectively, and superscript \('*'\) indicates the complex conjugate of the field.

We also calculated the normalised (relative) spectral intensity of the radiation collected through the pin hole:

**Top view:**
\[ I^n_T(\lambda_i) = \frac{I_T(\lambda_i)}{\sum_{i=0}^{11} I_T(\lambda_i)}, \quad i = 0, 1, 2, ..., 11; \quad (5a) \]

**Side view:**
\[ I^n_S(\lambda_i) = \frac{I_S(\lambda_i)}{\sum_{i=0}^{11} I_S(\lambda_i)}, \quad i = 0, 1, 2, ..., 11. \quad (5b) \]
FIG. 2. Four cases under consideration for the photon collections emitted from a single NV centre, which is represented by an electric dipole with moment $\mathbf{p}$, implemented in a spherical nanodiamond when the NV centre is located at different positions along the $x$-axis: (a) Case A, $\mathbf{p} = (p, 0, 0)$ and side view; (b) Case B, $\mathbf{p} = (p, 0, 0)$ and top view; (c) Case C, $\mathbf{p} = (0, 0, p)$ and side view; and (d) Case D, $\mathbf{p} = (0, 0, p)$ and side view.

The normalised spectra are important as there are often large experimental variations in total fluorescence and hence relative changes in the spectrum are often easier to observe.

III. RESULTS

To demonstrate how the position of the NV centre in a spherical nanodiamond can affect the photon collections at the far field, we locate the NV centre at varying positions along
FIG. 3. The overall photon counts (a) and (b) emitted from a NV centre embedded in a nanodiamond with radius of $a = 10$ nm when the NV colour centre is placed from the left to the right of the nanodiamond. Also, the normalised photon counts (c) and (d) at $x_d/a = 0$ for Case A and Case D, which almost fully represent the relative intensities of a NV centre in bulk diamond at the low-temperature condition listed in Table I.

The $x$-axis, $\mathbf{x}_d = (x_d, 0, 0)$ and $|x_d| = d$. The equivalent electric dipole moment, $\mathbf{p}$, can be either along $x$-axis or $z$-axis. Together with two observation spots, the top view and the side view, as shown in Fig. 2, we studied four cases: (i) Case A, $\mathbf{p} = (p, 0, 0)$ and side view; (ii) Case B, $\mathbf{p} = (p, 0, 0)$ and top view; (iii) Case C, $\mathbf{p} = (0, 0, p)$ and side view; and (iv) Case D, $\mathbf{p} = (0, 0, p)$ and side view. Corresponding to Case A to D, the animations of the overall
and normalised photon counts for $a = 10$ nm to $a = 300$ nm when the NV centre is located from the left to the right of the particle are presented in Supp. Mat. 1 to 4 and Supp. Mat. 5 to 8, respectively. Also, the detailed analysis for different size of particles is demonstrated below.

We start with the case of a small nanodiamond with a radius of $a = 10$ nm. When the particle size is small compared to the wavelength of the emitted light from the NV centre, the relative position of the NV centre to the surface of the diamond particle has insignificant effects on the photon collection by the optical objective (the pin hole) \cite{37}, as displayed in Fig. 3. In this figure, we only show the overall and normalised electromagnetic intensity profiles for Case A and Case D as a function of the number of de-exciting phonons, which almost fully represent the relative intensities of a NV centre in bulk diamond at the low-temperature condition listed in Table I. For Case B and Case C, the profiles are same as what are presented in Fig. 3 and hence are not shown in the main text.

When the radius of the diamond particle is 100 nm, the effects on the photon counts emitted from the NV centre due to its location relative to the nanodiamond surface start to present. For example, when the equivalent electric dipole moment direction is along the $x$-axis, the overall electromagnetic field intensity collected by the objective from side (Case A) and top (Case B) view is stronger when the dipole is located in the centre of the diamond particle relative to when it is close to the diamond surface, as shown in Fig. 4 (a) and (b) as well as in Fig. 5 (a) and (b). However, if the dipole moment direction is along the $z$-axis, the overall electromagnetic field intensity is stronger when the dipole is close to the diamond particle surface on the left for the side view, as shown in Fig. 4 (c) and 5 (c). With the top view for $z$-oriented NV centre, the overall electromagnetic field intensity profile is symmetric with respect to the centre of the diamond centre. The emission is weaker when the dipole is near the centre of the particle relative to when it is close to the particle surface, as displayed in Fig. 4 (d) and 5 (d).

In Fig. 6, the normalised electromagnetic field intensity profiles, $I_n^S$ and $I_n^T$, are shown for a diamond particle with radius of 100 nm. Compared to the overall electromagnetic field intensity, one obvious difference is that the effects of the NV centre location is less significant for the normalised intensity which is almost the same as the relative intensity of a NV centre in bulk diamond.

Nevertheless, when the diamond particle size is $a = 110$ nm, the effects of the location
FIG. 4. The overall photon counts (colour axis) emitted from a NV centre embedded in a nanodiamond with radius of $a = 100$ nm when the NV colour centre is placed from the left to the right of the nanodiamond. For the $x$-oriented dipole [(A) top view and (B) side view] the emission is brightest when $x_d/a \lesssim 0$. For the $z$-oriented dipole [(C) and (D)], emission is brightest towards the edges and exhibits different emission in the top (C) and side (D) directions. Note that the colour axes are different in each image.

of the NV centre on the normalised intensity become noticeable. As shown in Fig. 7 when the equivalent electric dipole moment direction is along the $z$-axis, the dominant signal of the normalised intensity is changed from $\lambda = 708$ nm to $\lambda = 683$ nm when the NV centre is close to the particle surface.
FIG. 5. The overall photon counts emitted from a NV centre embedded in a nanodiamond with radius of $a = 100$ nm at selected NV centre locations.

When the radius of the diamond particle is 200 nm, the subtle effects that were predicted for the 100 nm particles become far more pronounced. Large changes in both the overall and relative (normalised) spectra are observed. The spectra for the overall electromagnetic field intensity for the four cases are shown in Fig. 8 and 9. When the equivalent electric dipole moment direction is along the $x$-axis, the overall electromagnetic field intensity collected from both the top and side views indicate that, when the NV centre is deep in the nanodiamond particle, the fluorescence signals are much stronger than that when it is close to the particle.
FIG. 6. The normalised photon counts emitted from a NV centre embedded in a nanodiamond with radius of $a = 100\ \text{nm}$ when the NV colour centre is placed from the left to the right of the nanodiamond. When compared to the overall electromagnetic field intensity, the effects of the NV centre location is less significant for the normalised intensity for a nanodiamond particle which radius is $a = 100\ \text{nm}$.

surface, as shown in Fig. 8 (a-b) and 9 (a-b). Unlike the symmetric fluorescence profile from the top view, the nanodiamond is much brighter when the NV centre locates in the left part of the particle ($x_d/a < 0$) from the side view as shown in Fig. 8 (a) and the comparison between $x_d/a = -0.3$ and $x_d/a = 0.5$ in Fig. 9 (a). Whereas if the dipole moment direction is in $z$-direction, for example, Case C and D in Fig. 8 (c-d) and Fig. 9 (c-d), emission signals
FIG. 7. The normalised photon counts emitted from a NV centre embedded in a nanodiamond with radius of \( a = 110 \) nm for Case D (a) when the NV colour centre is placed from the left to the right of the nanodiamond and (b) at selected NV centre locations.

from the NV centre is significant when it is either close to the particle surface or near the centre of the diamond particle.

The normalised electromagnetic field intensity profiles of a single NV centre implemented in a nanodiamond with radius of \( 200 \) nm are shown in Fig. 10 and 11. For Case A when the dipole moment is along \( x \)-axis and the photon collection is along the side view, the normalised electromagnetic field intensity almost represents the relative intensities of a NV centre in bulk diamond when the NV centre is located in the left part of the nanodiamond particle \( (x_d/a < 0) \). Nevertheless, if the NV centre is placed to the right part in the nanodiamond when \( x_d/a > 0 \), compared to the relative intensities of a NV centre in bulk diamond, dominant wavelength of the normalised electromagnetic field intensity collected from the side view is firstly changes from \( \lambda = 708 \) nm to \( \lambda = 736 \) nm at around \( x_d/a = 0.5 \) and then changes again to \( \lambda = 659 \) nm at around \( x_d/a = 0.6 \), as shown in Fig. 10 (a) and 11 (a). Also, at \( x_d/a = 0.6 \), there is a second peak of the normalised electromagnetic field intensity at \( \lambda = 765 \) nm, while the signal at 708 nm is significantly reduced. Regarding to the top view as presented in Fig. 10 (b) and 11 (b) for Case B, the normalised electromagnetic field intensity profile is similar to that of a NV centre in bulk diamond when the NV centre is located from side to side in the particle. If the dipole moment direction is \( z \)-oriented,
FIG. 8. The overall photon counts emitted from a NV centre embedded in a nanodiamond with radius of \(a = 200\) nm when the NV colour centre is placed from the left to the right of the nanodiamond.

Both the side and top views show that the emission signal is enhanced significantly when the NV centre is close to the surface of the particle (\(|x_d|/a > 0.5\)) for the wavelength at \(\lambda = 708\) nm, as shown in Fig. 10 (c-d) and 11 (c-d). When the z-oriented NV centre is deep in the particle, from the side view, the dominant number of de-exciting phonons changes from three (\(\lambda = 708\) nm) to five (\(\lambda = 765\) nm) around \(x_d/a = 0.4\), as shown in Fig. 10 (c) and 11 (c).

As the diamond radius increases to 300 nm, the spectra become richer. This is because there are numerous opportunities for resonances over the various wavelengths. For a diamond
FIG. 9. The overall photon counts emitted from a NV centre embedded in a nanodiamond with radius of $a = 200$ nm at selected NV colour centre locations.

particle with radius of $300$ nm, if the equivalent electric dipole moment direction is in the $x$-direction, the overall electromagnetic field intensity at $\lambda = 708$ nm is much stronger when the NV centre is around $x_d/a = -0.5$ in the particle from the side view, as shown in Fig 12 (a) and 13 (a) for Case A. From the top view, the symmetric profile of the field intensity with respect to the particle centre is obtained when the NV centre is located from one side to the other of the particle, and the strongest fluorescence signal happens at $|x_d/a| = 0.55$ for $\lambda = 708$ nm, as shown in Fig 12 (b) and 13 (b) for Case B. When the dipole moment
FIG. 10. The normalised photon counts emitted from a NV centre embedded in a nanodiamond with radius of $a = 200$ nm when the NV colour centre is placed from the left to the right of the nanodiamond.

Direction is pointing along the $z$-axis, the highest fluorescence signal happens at $x_d/a = -0.4$ for $\lambda = 708$ nm from the side view, as shown in Fig 12 (c) and 13 (c), while from the top view as shown in Fig 12 (d), the electromagnetic field intensity profile is symmetric to the particle centre and the strongest appears at around $|x_d|/a = 0.4$ for $\lambda = 708$ nm and $\lambda = 736$ nm. Also, for these two cases, when $x_d/a = -0.75$ from the side view and $|x_d|/a = 0.85$ from the top view, there are two peaks of the fluorescence signals at $\lambda = 683$ nm and $\lambda = 832$ nm while the original peak signal at $\lambda = 708$ nm for a NV centre in bulk diamond is significantly reduced.
FIG. 11. The normalised photon counts emitted from a NV centre embedded in a nanodiamond with radius of $a = 200$ nm at selected NV colour centre location.

Fig 14 illustrates the normalised fluorescence signals when a NV centre is located at different position in a diamond particle with radius of 300 nm. For Case A and B when the electric dipole moment direction is along $x$-axis, the dominant emission fluorescence is the same as a NV centre in bulk diamond at $\lambda = 708$ nm when the NV centre locates close to the surface of the diamond particle, as shown in Fig 14 (a-b) and 15 (a-b). When the NV centre locates at $x_d/a = 0.3$, the dominant emission wavelength changes to $\lambda = 736$ nm, as shown in Fig. 15 (a). For Case C and D as the dipole moment direction is in $z$-direction, when
FIG. 12. The overall photon counts emitted from a NV centre embedded in a nanodiamond with radius of \( a = 300 \) nm when the NV colour centre is placed from the left to the right of the nanodiamond.

If the position of the NV centre is close to the surface of the diamond particle, the strongest emission happens at \( \lambda = 683 \) nm relative to a NV centre in bulk diamond at \( \lambda = 708 \) nm, as shown in Fig 14 (c) and (d). If the NV centre location locates deeper in the diamond particle at around \( x_d/a = 0.45 \), the dominant emission is changed to \( \lambda = 736 \) nm, as shown in Fig 14 (c-d) and 15 (c-d). Also, as shown in Fig. 15 (c-d), when \( x_d/a = -0.75 \) from the side view and at \( |x_d|/a = 0.8 \) from the top view for a z-oriented NV centre, there are the two peaks of the normalised fluorescence signals at \( \lambda = 683 \) nm and \( \lambda = 832 \) nm while the original peak signal at \( \lambda = 708 \) nm for a NV centre in bulk diamond is significantly reduced.
When comparing the fluorescence profiles from a 300 nm diamond to those from the smaller diamonds, the emission from longer wavelengths are enhanced in the 300 nm case. This is because the particle size at radius of 300 nm is comparable to the longer wavelengths when the high refractive index of diamond is taken into consideration, which leads to the enhanced cavity effects of the diamond particle for the emission at the higher order lines \[38\].
FIG. 14. The normalised photon counts emitted from a NV centre embedded in a nanodiamond with radius of $a = 300$ nm when the NV colour centre is placed from the left to the right of the nanodiamond.

**IV. CONCLUSION**

We performed theoretical modelling of the fluorescence profiles of a NV colour centre in a spherical nanodiamond, exploring the effects of the relative location, orientation, and nanodiamond size on the emission probabilities of NV centre together. Changes in the emission probabilities lead to variations in the expected fluorescence profile. Our calculations indicate that the effects of the relative location, orientation of NV centre on the fluorescence signals become noticeable when the particle radius is greater than around $a = 110$ nm and
FIG. 15. The normalised photon counts emitted from a NV centre embedded in a nanodiamond with radius of $a = 300$ nm at selected NV colour centre locations.

much profound for larger particles when $a = 200$ nm and $a = 300$ nm, with negligible effects below $a = 100$ nm. Our results indicate that the information of the exact geometry of NV-diamond system is critical to understand and control the fluorescence profile, which is of importance to optimise such systems for quantum bio-sensing applications.
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Appendix A: Solution for the electromagnetic fields emitted from a NV centre in a spherical diamond particle

The solution procedure to calculate the electromagnetic fields emitted from a NV centre in a spherical diamond particle is given. It is worth noting that to easily and clearly show the calculation procedure and apply the usual setup of a spherical coordinate system, the equivalent electric dipole for the NV centre is chosen to locate along the the axis of symmetry (z-axis) from which the polar angle is measured in this appendix. It is straightforward to use the solution given here to get the results presented in the main text via simple coordinate transform and rotation.

To obtain the electromagnetic field radiated from a single NV centre in a spherical diamond particle to the external domain, it is convenient to use the spherical coordinate system, \((r, \theta, \varphi)\), which origin is at the centre of the diamond particle. As shown in Fig. 16, we assign the symmetric axis is along the \(z\)-axis which is the polar angle \(\theta\) measured from. The equivalent electric dipole for the NV centre is positioned along the axis of symmetry at \(de_z = d \cos \theta e_r - d \sin \theta e_\theta\). Two situations are considered separately: (i) the vertical dipole when the dipole moment direction is along the symmetric axis (z-axis) as \(p = pe_z = p \cos \theta e_r - p \sin \theta e_\theta\) as shown in Fig. 16 (a) and detailed in Sec. A1 and (ii) the horizontal dipole when the dipole moment direction is perpendicular to \(z\)-axis as \(p = pe_x = p \sin \theta \cos \varphi e_r + p \cos \theta \cos \varphi e_\theta - p \sin \varphi e_\varphi\) as shown in Fig. 16 (b) and detailed in Sec. A2. Here, \(e_r, e_\theta, e_\varphi\) are the unit vector along \(r, \theta, \varphi\) direction in the spherical co-
FIG. 16. Sketch of the calculation model for the internal and external electromagnetic fields driven by an electric dipole embedded in a dielectric sphere.

ordinate system, respectively. All the other dipole location and polarisation scenarios, such as the cases presented in the main text, can be easily obtained through coordinate rotation and linear superposition from the above two basic cases.

In the spherical coordinate system, the Maxwell’s equations in Eq. (2) are in the form of

\[
\frac{1}{r \sin \theta} \left[ \frac{\partial}{\partial \theta} \left( E^j_r \sin \theta \right) - \frac{\partial E^j_\theta}{\partial \varphi} \right] = i \omega \mu_0 \mu_j H^j_r, \quad (A1a)
\]

\[
\frac{1}{r} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \left( E^j_\theta \right) - \frac{\partial}{\partial r} \left( r E^j_\varphi \right) \right] = i \omega \mu_0 \mu_j H^j_\theta, \quad (A1b)
\]

\[
\frac{1}{r} \left[ \frac{\partial}{\partial r} \left( r E^j_\varphi \right) - \frac{\partial E^j_\theta}{\partial \theta} \right] = i \omega \mu_0 \mu_j H^j_\varphi, \quad (A1c)
\]

\[
\frac{1}{r \sin \theta} \left[ \frac{\partial}{\partial \theta} \left( H^j_\varphi \sin \theta \right) - \frac{\partial H^j_\theta}{\partial \varphi} \right] = -i \omega \epsilon_0 \epsilon_j E^j_r, \quad (A2a)
\]

\[
\frac{1}{r} \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \left( H^j_\theta \right) - \frac{\partial}{\partial r} \left( r H^j_\varphi \right) \right] = -i \omega \epsilon_0 \epsilon_j E^j_\theta, \quad (A2b)
\]

\[
\frac{1}{r} \left[ \frac{\partial}{\partial r} \left( r H^j_\varphi \right) - \frac{\partial H^j_\theta}{\partial \theta} \right] = -i \omega \epsilon_0 \epsilon_j E^j_\varphi, \quad (A2c)
\]

In the above equation, the continuity equations of the electric and magnetic fields are not
given as they are satisfied straightforwardly when the Mie solution procedure is used, as demonstrated below.

Before we solve for the reflection and radiation electromagnetic fields in Domain 1 and 2, we need to write the fields due to the electric dipole in the spherical coordinate system. From Eq. (1), we have

\[
E^d = \frac{1}{4\pi\varepsilon_0\varepsilon_r} \left\{ (-k_2 r_d^2 - 3i k_2 r_d + 3) \frac{r_d \cdot p}{r_d^2} r_d + (k_2 r_d^2 + i k_2 r_d - 1)p \right\}
\]

\[
= \frac{1}{4\pi\varepsilon_0\varepsilon_r} \left[ p \nabla^2 G(x, x_d) - (p \cdot \nabla) \nabla G(x, x_d) \right], \tag{A3a}
\]

\[
H^d = \frac{\omega k_2}{4\pi} [r_d \times p] \left\{ \frac{1}{r_d} - \frac{1}{i k_2 r_d^2} \right\} \frac{\exp(i k_2 r_d)}{r_d}
\]

\[
= -\frac{i\omega}{4\pi} [\nabla G(x, x_d) \times p] \tag{A3b}
\]

where \( G(x, x_d) \) is the Green’s function for the Helmholtz equation as

\[
G(x, x_d) = \frac{\exp(i k_2 |x - x_d|)}{|x - x_d|}. \tag{A4}
\]

As shown in Fig. 16, \( r_d \equiv |x - x_d| = \sqrt{r^2 + d^2 - 2rd\cos\theta} \) based on the cosine theorem. In this case, the free space Green’s function for the Helmholtz equation can be rewritten in terms of \((r, d, \theta)\) and asymptotically represented in terms of free spherical multipolar waves, respectively, as

\[
G(x, x_d) \equiv G(r, \theta; d) = \frac{\exp \left( i k_2 \sqrt{r^2 + d^2 - 2rd\cos\theta} \right)}{\sqrt{r^2 + d^2 - 2rd\cos\theta}} \tag{A5}
\]

\[
= i k_2 \sum_{n=0}^{N} (2n + 1) h_n^{(1)}(k_2 r_>) j_n(k_2 r_<) P_n(\cos\theta) \tag{A6}
\]

where \( r_> \equiv \max(|x|, d), r_< \equiv \min(|x|, d) \), and \( N = k_1 a + 4(k_1 a)^{1/3} + 2 \) is the transacted number for the summation \([33]\). Introducing Eq. (A5) or Eq. (A6) into Eq. (A3) and using the vector calculus formulae in the spherical coordinate system, the fields due to the electric dipole in the spherical coordinate system are obtained.

1. **Vertical electric dipole**

Let us firstly consider to solve for the electromagnetic fields as the case illustrated in Fig. 16 (a). Introducing Eq. (A5) into Eq. (A3) and using the vector calculus formulae
in the spherical coordinate system, the electric and magnetic fields induced by a vertical electric dipole, when \( p = p \cos \theta \mathbf{e}_r - p \sin \theta \mathbf{e}_\theta \), are

\[
E^d_r = \frac{1}{4\pi \epsilon_0 \epsilon_r} \frac{p}{d} \left\{ \frac{\partial^2 [r G(r, \theta; d)]}{\partial r^2} + k^2 r G(r, \theta; d) \right\}, \quad (A7a)
\]

\[
E^d_\theta = \frac{1}{4\pi \epsilon_0 \epsilon_r} \frac{p}{rd} \frac{\partial^2 [r G(r, \theta; d)]}{\partial r \partial \theta}, \quad (A7b)
\]

\[
E^d_\varphi = 0; \quad (A7c)
\]

\[
H^d_r = 0, \quad (A7d)
\]

\[
H^d_\theta = 0, \quad (A7e)
\]

\[
H^d_\varphi = -\frac{i \omega p}{4\pi d} \frac{\partial G(r, \theta; d)}{\partial \theta}. \quad (A7f)
\]

Based on the Mie theory [31] by using Debye potentials \( u \) and \( v \) that satisfy the Helmholtz equation [32, 33], we can write the electric and magnetic fields as

\[
E = E_0 (M_v - iN_u), \quad (A8a)
\]

\[
H = E_0 \sqrt{\frac{\epsilon_0 \epsilon_r}{\mu_0 \mu_r}} (-iN_v - M_u) \quad (A8b)
\]

where \( E_0 = p/(4\pi \epsilon_0 a^3) \),

\[
M_u = \nabla \times (ru), \quad M_v = \nabla \times (rv), \quad (A9a)
\]

\[
\nabla \times M_u = \omega (\epsilon_0 \epsilon_r \mu_0 \mu_r)^{\frac{1}{2}} N_u, \quad \nabla \times M_v = \omega (\epsilon_0 \epsilon_r \mu_0 \mu_r)^{\frac{1}{2}} N_v, \quad (A9b)
\]

\[
\nabla \times N_u = \omega (\epsilon_0 \epsilon_r \mu_0 \mu_r)^{\frac{1}{2}} M_u, \quad \nabla \times N_v = \omega (\epsilon_0 \epsilon_r \mu_0 \mu_r)^{\frac{1}{2}} M_v, \quad (A9c)
\]

\[
\nabla \times E = i \omega \mu_0 \mu_r H, \quad \nabla \times H = -i \omega \epsilon_0 \epsilon_r E. \quad (A9d)
\]

The full components of \( M_u \) and \( N_u \) are, respectively,

\[
M_{u_r} = 0, \quad M_{u_\theta} = \frac{1}{r \sin \theta} \frac{\partial (ru)}{\partial \varphi}, \quad M_{u_\varphi} = -\frac{1}{r} \frac{\partial (ru)}{\partial \theta}; \quad (A10a)
\]

\[
N_{u_r} = \frac{1}{k} \frac{\partial^2 (ru)}{\partial r^2} + kr, \quad N_{u_\theta} = \frac{1}{kr} \frac{\partial^2 (ru)}{\partial r \partial \theta}, \quad N_{u_\varphi} = \frac{1}{kr \sin \theta} \frac{\partial^2 (ru)}{\partial r \partial \varphi}. \quad (A10b)
\]

The above formulations can also be used to get the components of \( M_v \) and \( N_v \) when potential \( u \) is replaced by potential \( v \).

As Debye potentials \( u \) and \( v \) satisfy the Helmholtz equation, let us consider a scalar wave equation for function \( \phi \) with wavenumber \( k \):

\[
\nabla^2 \phi + k^2 \phi = 0 \quad (A11)
\]
where $\phi$ represents either potential $u$ or $v$. Eq. (A11) is variable separable in the spherical coordinate system, and its elementary solutions are

\[
\phi(l,n) = \sum_{n=0}^{\infty} \sum_{l=-n}^{n} C_{l,n} \cos(l\varphi) P_n^l(\cos \theta) z_n(kr), \quad \text{(A12a)}
\]

\[
\phi(l,n) = \sum_{n=0}^{\infty} \sum_{l=-n}^{n} D_{l,n} \sin(l\varphi) P_n^l(\cos \theta) z_n(kr), \quad \text{(A12b)}
\]

where $l$ and $n$ are integers ($n \geq l \geq 0$), $P_n^l(\cos \theta)$ is an associated Legendre polynomial, and $z_n(kr)$ is the spherical Bessel function of any kind. The following rules are applied to determine the choice of function $z_n(kr)$. In the bounded domain with origin within it, $j_n(kr)$, the spherical Bessel function of the first kind, is used as $j_n(kr)$ is finite at origin. In the bounded domain excluding origin, both $j_n(kr)$ and $y_n(kr)$, the spherical Bessel functions of the first and second kinds, are needed. In the unbounded external domain, for the scattered or radiation field, $h_n^{(1)} = j_n(kr) + iy_n(kr)$ is used as $ik h_n^{(1)} \sim i^n \exp(ikr)/r$.

It is worth noting that the two Debye potentials, $u$ and $v$, correspond to $\cos(l\varphi)$ and $\sin(l\varphi)$ formulations in Eq. (A12), respectively. Nevertheless, according to Eq. (A7), the fields driven by a vertical electric dipole in a sphere do not depend on $\varphi$. As such, only terms with $l = 0$ in Eq. (A12) are needed, which means only one potential is needed for each domain. Let us use potential $u$:

\[
u^1_{(0,n)} = \sum_{n=0}^{N} C_{(0,n)}^1 P_n(\cos \theta) h_n^{(1)}(k_1r) \quad \text{external domain,} \quad \text{(A13a)}
\]

\[
u^2_{(0,n)} = \sum_{n=0}^{N} C_{(0,n)}^2 P_n(\cos \theta) j_n(k_2r) \quad \text{internal domain} \quad \text{(A13b)}
\]

where the $C_{(0,n)}^1$ and $C_{(0,n)}^2$ are determined by the boundary conditions. Introducing
Eq. (A13) into Eq. (A8) and using Eq. (A10), we obtain

\[E_r^1 = E_0 \sum_{n=0}^{N} C_{(0,n)}^1 (-i) \frac{n(n+1)}{k_1 r} h_n^{(1)}(k_1 r) P_n(\cos \theta),\]  

(A14a)

\[E_\theta^1 = E_0 \sum_{n=0}^{N} C_{(0,n)}^1 (-i) \frac{1}{k_1 r} [(n+1)h_n^{(1)}(k_1 r) - k_1 r h_{n+1}^{(1)}(k_1 r)] P_n^1(\cos \theta),\]  

(A14b)

\[E_\phi = 0;\]  

(A14c)

\[H_r^1 = 0,\]  

(A14d)

\[H_\theta^1 = 0,\]  

(A14e)

\[H_\phi = \frac{E_0}{\omega \mu_0} \sum_{n=0}^{N} C_{(0,n)}^1 \frac{k_1}{\mu_2} h_n^{(1)}(k_1 r) P_n^1(\cos \theta).\]  

(A14f)

Also,

\[E_r^2 = E_0 \sum_{n=0}^{N} C_{(0,n)}^2 (-i) \frac{n(n+1)}{k_2 r} j_n(k_2 r) P_n(\cos \theta),\]  

(A15a)

\[E_\theta^2 = E_0 \sum_{n=0}^{N} C_{(0,n)}^2 (-i) \frac{1}{k_2 r} [(n+1)j_n(k_2 r) - k_2 r j_{n+1}(k_2 r)] P_n^1(\cos \theta),\]  

(A15b)

\[E_\phi = 0;\]  

(A15c)

\[H_r^2 = 0,\]  

(A15d)

\[H_\theta^2 = 0,\]  

(A15e)

\[H_\phi = \frac{E_0}{\omega \mu_0} \sum_{n=0}^{N} C_{(0,n)}^2 \frac{k_2}{\mu_2} j_n(k_2 r) P_n^1(\cos \theta).\]  

(A15f)

To get \(C_{(0,n)}^1\) and \(C_{(0,n)}^2\), the boundary conditions across the sphere surface:

\[E_\theta^1 = E_\theta^2 + E_\phi^d \quad \text{when} \quad r = a,\]  

(A16a)

\[H_\phi^1 = H_\phi^2 + H_\phi^d \quad \text{when} \quad r = a\]  

(A16b)

are used. Introducing Eq. (A6) into Eq. (A7) and setting \(r = a\), we have

\[E_\theta^d \bigg|_{r=a} = \frac{1}{4\pi \epsilon_0 \epsilon_2} \frac{p}{ad} i k_2 \sum_{n=0}^{N} (2n+1) j_n(k_2 d) P_n^1(\cos \theta) \frac{d}{dr} \left[ r h_n^{(1)}(k_2 r) \right] \bigg|_{r=a},\]  

(A17a)

\[H_\phi^d \bigg|_{r=a} = -\frac{i \omega p}{4\pi d} i k_2 \sum_{n=0}^{N} (2n+1) h_n^{(1)}(k_2 a) j_n(k_2 d) P_n^1(\cos \theta).\]  

(A17b)
Letting $r = a$ in Eqs. (A14) and (A15), and introducing the results and Eq. (A17) into Eq. (A16), we obtain a $2 \times 2$ linear system to solve for the unknown coefficients $C^1_{(0,n)}$ and $C^2_{(0,n)}$ which can be then introduced into Eqs. (A14) and (A15) to calculate the fields inside, outside the sphere and on the sphere surface.

2. Horizontal electric dipole

Let us turn to solve for the electromagnetic fields as the case illustrated in Fig. 16(b). Introducing Eq. (A5) into Eq. (A3) and using the vector calculus formulae in the spherical coordinate system, the radial components of the electric and magnetic fields induced by a horizontal electric dipole when $p = p \sin \theta \cos \varphi e_r + p \cos \theta \cos \varphi e_\theta - p \sin \varphi e_\varphi$ are

$$E^d_r = -\frac{1}{4\pi \varepsilon_0 \varepsilon_r} \frac{p}{r} \frac{\partial}{\partial \theta} \left\{ \frac{\partial [G(r, \theta; d)]}{\partial d} + \frac{1}{d} G(r, \theta; d) \right\} \cos \varphi, \quad (A18a)$$

$$H^d_r = \frac{i\omega}{4\pi} \frac{p}{r} \frac{\partial G(r, \theta; d)}{\partial \theta} \sin \varphi. \quad (A18b)$$

Following the same solution procedure shown in the previous section and considering that the electromagnetic fields given in Eq. (A18) are functions of $\sin \varphi$ and $\cos(\varphi)$, only the terms when $l = 1$ from the elementary solutions in Eq. (A12) are needed for the Debye potentials. As such, the following Debye potentials

$$u^1_{(1,n)} = \cos \varphi \sum_{n=1}^{N} C^1_{(1,n)} h^{(1)}_n(k_1 r) P^1_n(\cos \theta) \quad \text{external domain}, \quad (A19a)$$

$$v^1_{(1,n)} = -\sin \varphi \sum_{n=1}^{N} D^1_{(1,n)} h^{(1)}_n(k_1 r) P^1_n(\cos \theta) \quad \text{external domain}; \quad (A19b)$$

$$u^2_{(1,n)} = \cos \varphi \sum_{n=1}^{N} C^2_{(1,n)} j_n(k_1 r) P^1_n(\cos \theta) \quad \text{internal domain}, \quad (A19c)$$

$$v^2_{(1,n)} = -\sin \varphi \sum_{n=1}^{N} D^2_{(1,n)} j_n(k_1 r) P^1_n(\cos \theta) \quad \text{internal domain} \quad (A19d)$$

are used where $C^1_{(1,n)}$, $D^1_{(1,n)}$, $C^2_{(1,n)}$, $D^2_{(1,n)}$ are unknowns to be determined via boundary conditions.
Introducing Eq. (A19) into Eq. (A8) and using Eq. (A10), we obtain

\[ E_r^1 = E_0 \cos \varphi \sum_{n=1}^{N} C_{(1,n)}^1 (-i) \frac{n(n+1)}{k_1 r} h_n^{(1)}(k_1 r) P_n^1(\cos \theta), \]  
(A20a)

\[ E_\theta^1 = E_0 \cos \varphi \sum_{n=1}^{N} C_{(1,n)}^1 (-i) \frac{1}{k_1 r} \left[ (n + 1) h_n^{(1)}(k_1 r) - k_1 r h_n^{(1)}(k_1 r) \right] \frac{P_n^1(\cos \theta)}{\sin \theta} + E_0 \cos \varphi \sum_{n=1}^{N} D_{(1,n)}^1 (-1) h_n^{(1)}(k_1 r) \frac{P_n^1(\cos \theta)}{k_1 r} \]  
(A20b)

\[ E_\varphi^1 = E_0 \sin \varphi \sum_{n=1}^{N} C_{(1,n)}^1 (i) \frac{1}{k_1 r} \left[ (n + 1) h_n^{(1)}(k_1 r) - k_1 r h_n^{(1)}(k_1 r) \right] \frac{P_n^1(\cos \theta)}{\sin \theta} + E_0 \sin \varphi \sum_{n=1}^{N} D_{(1,n)}^1 h_n^{(1)}(k_1 r) \frac{dP_n^1(\cos \theta)}{d\theta} \]  
(A20c)

and

\[ H_r^1 = \frac{E_0}{\omega \mu_0} \sin \varphi \sum_{n=1}^{N} D_{(1,n)}^1 (i) \frac{k_1}{\mu_1} \frac{n(n+1)}{k_1 r} h_n^{(1)}(k_1 r) P_n^1(\cos \theta), \]  
(A21a)

\[ H_\theta^1 = \frac{E_0}{\omega \mu_0} \sin \varphi \sum_{n=1}^{N} C_{(1,n)}^1 \frac{k_1}{\mu_1} h_n^{(1)}(k_1 r) \frac{P_n^1(\cos \theta)}{\sin \theta} + \frac{E_0}{\omega \mu_0} \sin \varphi \sum_{n=1}^{N} D_{(1,n)}^1 (i) \frac{k_1}{\mu_1} \frac{1}{k_1 r} \left[ (n + 1) h_n^{(1)}(k_1 r) - k_1 r h_n^{(1)}(k_1 r) \right] \frac{dP_n^1(\cos \theta)}{d\theta} \]  
(A21b)

\[ H_\varphi^1 = \frac{E_0}{\omega \mu_0} \cos \varphi \sum_{n=1}^{N} C_{(1,n)}^1 \frac{k_1}{\mu_1} h_n^{(1)}(k_1 r) \frac{dP_n^1(\cos \theta)}{d\theta} + \frac{E_0}{\omega \mu_0} \cos \varphi \sum_{n=1}^{N} D_{(1,n)}^1 (i) \frac{k_1}{\mu_1} \frac{1}{k_1 r} \left[ (n + 1) h_n^{(1)}(k_1 r) - k_1 r h_n^{(1)}(k_1 r) \right] \frac{P_n^1(\cos \theta)}{\sin \theta}. \]  
(A21c)
Also

\[ E_r^2 = E_0 \cos \phi \sum_{n=1}^{N} C_{(1,n)}^2 (-i) \frac{n(n+1)}{k_2 r} j_n(k_2 r) P_n^1(\cos \theta), \]  
\( \text{(A22a)} \)

\[ E_\theta^2 = E_0 \cos \phi \sum_{n=1}^{N} C_{(1,n)}^2 (-i) \frac{1}{k_2 r} [(n+1)j_n(k_2 r) - k_2 r j_{n+1}(k_2 r)] \frac{dP_n^1(\cos \theta)}{d\theta}, \]  
\( \text{(A22b)} \)

\[ E_\phi^2 = E_0 \sin \phi \sum_{n=1}^{N} C_{(1,n)}^2 (i) \frac{1}{k_2 r} [(n+1)j_n(k_2 r) - k_2 r j_{n+1}(k_2 r)] \frac{P_n^1(\cos \theta)}{\sin \theta}, \]  
\( \text{(A22c)} \)

and

\[ H_r^1 = \frac{E_0}{\omega \mu_0} \sin \phi \sum_{n=1}^{N} D_{(1,n)}^2 (i) \frac{k_2 n(n+1)}{\mu_2 k_2 r} j_n(k_2 r) P_n^1(\cos \theta), \]  
\( \text{(A23a)} \)

\[ H_\theta^1 = \frac{E_0}{\omega \mu_0} \sin \phi \sum_{n=1}^{N} C_{(1,n)}^2 \frac{k_2 j_n(k_2 r)}{\mu_2 k_2 r} P_n^1(\cos \theta) \frac{dP_n^1(\cos \theta)}{d\theta}, \]  
\( \text{(A23b)} \)

\[ H_\phi^1 = \frac{E_0}{\omega \mu_0} \cos \phi \sum_{n=1}^{N} C_{(1,n)}^2 \frac{k_2 j_n(k_2 r)}{\mu_2 k_2 r} \frac{dP_n^1(\cos \theta)}{d\theta}, \]  
\( \text{(A23c)} \)

Once the coefficients \( C_{(1,n)}^1, D_{(1,n)}^1, C_{(1,n)}^2, D_{(1,n)}^2 \) are found, the electromagnetic fields in both domains are determined. To get those coefficients, the boundary conditions for the tangential components of the electric and magnetic fields due to electric dipole on the sphere surface when \( r = a \) are need, which can be found by using the Maxwell’s equations and the radial components in Eq. \( \text{(A18)} \). Introducing Eq. \( \text{(A1b)} \) in Eq. \( \text{(A2c)} \), for the sphere domain, we get

\[ \frac{\partial^2}{\partial r^2} (r E_\phi^d) + k_2^2 (r E_\phi^d) = \frac{1}{\sin \theta} \frac{\partial}{\partial r} \left( \frac{\partial E_\phi^d}{\partial \varphi} \right) - i \omega \mu_0 \mu_2 \frac{\partial H_\phi^d}{\partial \theta}. \]  
\( \text{(A24)} \)

The right-hand-side of Eq. \( \text{(A24)} \) can be obtained by using the results from introducing
As such, in which the situation for the fields on the sphere surface when $r \to a > d$ is implied. When comparing the left-hand-side of Eq. (A24) and Eqs. (A25) and (A26), we notice that we can get the tangential component, $E^d_\varphi$, by solving the following two ordinary differential equations:

$$\frac{d^2 g_1(r)}{dr^2} + k_2^2 g_1(r) = \frac{1}{n(n+1)} \left( (n+1)j_n(k_2r) - k_2d j_{n+1}(k_2d) \right) \frac{P_n^1(\cos \theta)}{\sin \theta}, \quad (A27)$$

and

$$\frac{d^2 g_2(r)}{dr^2} + k_2^2 g_2(r) = \frac{h_n^{(1)}(k_2r)}{r}. \quad (A28)$$

The solutions to the above two equations are, respectively,

$$g_1(r) = \frac{1}{n(n+1)} \frac{d}{dr} \left[ r h_n^{(1)}(k_2r) \right] = \frac{1}{n(n+1)} \left[ (n+1)h_n^{(1)}(k_2r) - k_2 r h_n^{(1)}(k_2r) \right], \quad (A29)$$

$$g_2(r) = \frac{1}{n(n+1)} r h_n^{(1)}(k_2r). \quad (A30)$$

As such,

$$E^d_\varphi = \frac{p \sin \varphi \ i k_2}{4\pi \epsilon_0 \epsilon_2 \ r d} \sum_{n=1}^{N} \frac{2n+1}{n(n+1)} \frac{d}{dr} \left[ r h_n^{(1)}(k_2r) \right] \left[ (n+1)j_n(k_2d) - k_2d j_{n+1}(k_2d) \right] \frac{P_n^1(\cos \theta)}{\sin \theta}$$

\[+\frac{p \sin \varphi \ i k_2}{4\pi \epsilon_0 \epsilon_2 \ r d} \sum_{n=1}^{N} \frac{2n+1}{n(n+1)} h_n^{(1)}(k_2r) j_n(k_2d) \frac{dP_n^1(\cos \theta)}{d\theta}. \quad (A31)\]

Introducing Eq. (A6) into Eq. (A18) and substituting that result and Eq. (A31) into Eq. (A1b), we have

$$H^d_\theta = \frac{1}{i \omega \mu_0 \mu_2} \left[ \frac{1}{r \sin \theta} \frac{\partial E^d_\varphi}{\partial \varphi} - \frac{1}{r} \frac{\partial (r E^d_\varphi)}{\partial r} \right]$$

\[= \frac{p \omega \sin \varphi \ i k_2}{4\pi \ r d} \sum_{n=1}^{N} \frac{2n+1}{n(n+1)} k_2 r h_n^{(1)}(k_2r) \left[ (n+1)j_n(k_2d) - k_2d j_{n+1}(k_2d) \right] \frac{P_n^1(\cos \theta)}{\sin \theta} \]

\[\quad- \frac{p \omega \sin \varphi \ k_2^2}{4\pi \ r} \sum_{n=1}^{N} \frac{2n+1}{n(n+1)} \frac{d}{dr} \left[ r h_n^{(1)}(k_2r) \right] j_n(k_2d) \frac{dP_n^1(\cos \theta)}{d\theta}. \quad (A32)\]
FIG. 17. Good agreement has been found for the electromagnetic fields between the results obtained by the asymptotic approximations shown in Section A (solid lines), by the in-house built field only surface integral method \[35\] (symbols) when \(a = 200 \text{ nm}, \ d = 50 \text{ nm}, \ n_1 = 1, \ n_2 = 2.4, \ E_0 = p/(4\pi\epsilon_0a^3)\) and \(\lambda = 708 \text{ nm}\): (a) a vertical electric dipole and (b) a horizontal electric dipole. The curves plotted are the magnitudes of the electromagnetic fields along the circle concentric with the spherical particle with radius as \(4a\) on the \(xz\) plane (as shown in the inset of Fig. 17a).

As the tangential components of the electric and magnetic fields are continuous across the sphere surface, we have

\[
\begin{align*}
E^1_\phi &= E^2_\phi + E^d_\phi \quad &\text{when } r = a, \\
H^1_\theta &= H^2_\theta + H^d_\theta \quad &\text{when } r = a.
\end{align*}
\]

(A33a)  
(A33b)

Comparing the expressions in Eqs. (A20c), (A21b), (A22c), (A23b) and those in Eqs. (A31), (A32), we obtain a \(4 \times 4\) linear system to solve for the unknown coefficients \(C^1_{(1,n)}, \ D^1_{(1,n)}, \ C^2_{(1,n)}\) and \(D^2_{(1,n)}\) that can be introduced back into Eqs. (A20) and (A23) to calculate the fields inside, outside the sphere and on the sphere surface.

In Fig. 17, we showed the electromagnetic fields obtained by the asymptotic approximations detailed in Section A and compared them with the results gotten by the in-house built field only surface integral method \[35\]. Good agreement has been found between the results
obtained by the different methods mentioned above.

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