Selection rule engineering of forbidden transitions of a hydrogen atom near a nanogap

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Abstract: We perform an analytical study on the allowance of forbidden transitions for a hydrogen atom placed near line dipole sources, mimicking light emanating from a one-dimensional metallic nanogap. It is shown that the rapid variation of the electric field vector, inevitable in the near zone, completely breaks the selection rule of \( \Delta l = \pm 1 \). While the forbidden transitions between spherically symmetric S states, such as 2S to 1S or 3S to 1S (\( \Delta l = 0 \)), are rather robust against selection rule breakage, \( \Delta l = \pm 2 \) transitions such as between 3D and 1S or 3D and 2S states are very vulnerable to the spatial variation of the perturbing electric field. Transitions between 2S and 3D states are enhanced by many orders of magnitude, aided by the quadratic nature of both the perturbing Hamiltonian and D wavefunctions. The forbidden dipole moment, which approaches one Bohr radius times the electric charge in the vicinity of the gap, can be written in a simple closed form owing to the one-dimensional nature of our gap. With large enough effective volume together with the symmetric nature of the excited state wavefunctions, our work paves way towards atomic physics application of infinitely long nanogaps.

Keywords: nanogap; selection rule; forbidden transition; quantum plasmonics.

1 Introduction

Long wavelength approximation is at the heart of well-known selection rules in atomic spectroscopy. The wavelength of light is much larger than the atom size, so that the light-atom interaction Hamiltonian can safely ignore the spatial variation in the scale of the wavelength, resulting in an effective Hamiltonian in the form of

\[-\mathbf{p} \cdot \mathbf{E} = -e\hat{x} \cdot \mathbf{E}e^{-i\omega t}\]

where \( \mathbf{p} \) is the dipole moment operator, \( \mathbf{E} \) the electric field of light, \( \hat{x} \) the polarization direction unit vector, \( E_0 \) the amplitude of the electric field, and \( \omega \) the angular frequency of light. Thereby, spontaneous emission, stimulated emission, and absorption are all proportional to the matrix element \( \langle \psi_f | \hat{x} | \psi_i \rangle \) (\( \psi_f \), final and initial state wavefunctions, respectively), from which all selection rules follow. The most important selection rule \( \Delta l = \pm 1; \Delta m = \pm 1 \) originates from the position operator \( \hat{x} \) being represented by the spherical harmonics of order 1. While this selection rule can be broken by magnetic dipole transition, electric quadrupole transition, or by two photon transitions, these forbidden transitions are typically several orders of magnitudes weaker. For instance, the 2P-1S allowed transition lifetime of 2 ns for a hydrogen atom compares favorably with 4.6 days for the forbidden magnetic dipole transition lifetime of 2S to 1S. On the other hand, the electric quadrupole transition between 3D and 2S is somewhat less forbidden, taking 20 ms [1, 2]. Of some practical importance, this one-photon lifetime of the forbidden magnetic dipole transition between 2S and 1S is so impractically long that it is easily superseded by the two-photon lifetime of 0.15 s [3], which played an important role in the measurements of the Lamb shift [4].

While the spatial variation of electromagnetic waves in free space occurs within the wavelength scale, close to the induced sources such as surface current and surface charges which naturally occur in metallic nano objects, electric field vectors can vary in length scale much smaller than their vacuum wavelength, in the length scale of the nano objects themselves or the gap size between the metallic objects [5–19]. Of particular interest in the present paper is the one-dimensional metallic nano- and sub-nanogaps whose widths can be in the 1–0.1 nm regime [17–19], comparable to the spatial extents of hydrogen atom wavefunctions while maintaining a macroscopic length of 1 mm to 1 cm. Electric fields emanating from these gaps possess rapidly varying electric fields, both in magnitude and in direction, in the length scale of the gap itself, creating a potentially very useful field configuration for the
purpose of breaking down well-known selection rules, thereby facilitating forbidden transitions in large enough volumes to be experimentally detectable.

2 Materials and methods

To model spatial variation of the electric field emanating from nano- and sub-nanometer gaps, we first consider a line dipole with a line charge density $\lambda$ and a gap width of $w$, fed by an alternating current source of angular frequency $\omega$ and surface current density $K e^{i \omega t}$ with the charge conservation relationship $K = i \omega \lambda$. In the extreme subwavelength regime of our interest, we can ignore the retarded time, so that the electric field is approximated by the near-field term only [20–26]:

$$
\vec{E}(x,z,t) = \frac{\lambda e^{-i \omega t}}{2\pi \varepsilon_0} \left( \frac{\vec{r}_1 - \vec{r}_2}{r_1 r_2} \right) = \\
\frac{\lambda e^{-i \omega t}}{2\pi \varepsilon_0} \left( \frac{x - \frac{w}{2} z}{w^2 + z^2} - \frac{x + \frac{w}{2} z}{w^2 + z^2} \right),
$$

as plotted in Figure 1A for $w=1$ nm. By replacing $\lambda$ with $\sigma dz$ and integrating over a film thickness of $h=100$ nm, we obtain a realistic field profile of a capacitative nanogap of surface charge density $\sigma$, as shown in Figure 1B. For large

![Figure 1](image-url)

**Figure 1:** (A) Electric field lines above a line dipole of gap width 1 nm. Line charges are located at $x=\pm0.5$ nm, $z=0$. (B) Electric field profile obtained by an integration of the line dipoles from $z=-100$ to 0 nm, well fitted with an analytical form $\vec{E}(x,z) = \frac{\sigma w}{2\pi \varepsilon_0} \frac{(z-x)}{x^2 + z^2}$ when far away from the gap. (C) Electric field lines $\vec{E}(x,z) - \vec{E}(x_0, z)$ around a center position of $(x_0, z_0) = (3$ nm, 3 nm) together with $|\psi_{320}(x_0, z)|^2$. The color scale is in arbitrary units and we use the integrated field profile of Eq. (2). (D) Contour plot of an $xz$ cross section of the overlap integrand $\langle H^{(2)}_{320} | \psi_{320} \rangle$ around the center position of $(x_0, z_0)$ (3 nm, 3 nm). The color scale is in arbitrary units.
enough \( h \ll w \), this field is well approximated by a simple form:

\[
\vec{E}(x, z, t) = \frac{\sigma \omega}{2\pi \epsilon_0} \frac{(z - x)}{x^3 + z^3} e^{-i\omega t} \tag{2}
\]

for distances larger than \( w \) but smaller than \( h \). Unless otherwise indicated, calculations are performed using the integrated field profile of Eq. (2) using Mathematica and Matlab.

### 3 Results

We now place a hydrogen atom at a position \((x_o', z_o')\) in a field profile given as Eq. (3), and ask how the transition rates between different states will change relative to the case of a plane wave excitation. Near the source, say, at a position of \((x_o', z_o') = (3 \text{ nm}, 3 \text{ nm})\), the field lines are curved in the scale of the 3D wavefunctions of a hydrogen atom. It behooves us to examine the behavior of the electric field and the interaction Hamiltonian at the near field. Plotted in Figure 1C at \((x_o', z_o') = (3 \text{ nm}, 3 \text{ nm})\) are the electric field lines minus their central value, \(\vec{E}(x, z) - \vec{E}(x_o, z_o)\), with an \(xz\) cross section of the 3D wavefunction \(|\psi_{320}\rangle\) (\(n = 3\); \(l = 2\); \(m = 0\)) in an area of 2 nm by 2 nm squared. The field lines approximate those of a vector field \((x', z')\), with \((x, z) = (x_o + x', z_o + z')\), producing an interaction Hamiltonian with a symmetry of \(x'z'\), as can be seen clearly when we expand around \((x_o, z_o)\):

\[
H_{\text{int}} = e\phi(x, z) - e\phi(x_o, z_o) = e\sum_{n=1}^{\infty} \frac{1}{n}\left(\frac{\partial}{\partial x'} x' + \frac{\partial}{\partial z'} z'\right)^{n}\phi(x' + x_o', z' + z_o) \bigg|_{(x_o, z_o)} = H_{\text{int}}^{(1)} + H_{\text{int}}^{(2)} + \cdots, \tag{3}
\]

where \(e\) is the electron charge.

The first term is the dipole approximation Hamiltonian that gives rise to the usual selection rules, whereas the second term contains all the salient features:

\[
H_{\text{int}}^{(1)} = e \left(\frac{x'}{2\partial x'} + \frac{z'}{2\partial z'}\right)^2 \phi(x' + x_o', z' + z_o) \bigg|_{(x_o, z_o)}
\]

\[
e(\frac{x'^2 - z'^2}{2}) \frac{\partial E_z}{\partial z} \bigg|_{(x_o, z_o)} - ex'z' \frac{\partial E_z}{\partial x} \bigg|_{(x_o, z_o)} \tag{4}
\]

having taken advantage of the divergence relation \(\frac{\partial E_z}{\partial x} + \frac{\partial E_z}{\partial z} = 0\). To see how this Hamiltonian consisting of two-dimensional quadratic polynomials can be taken advantage of by the D waves, we resume our interest in the 2S to 3D transition. With the photon energy of 13.6 eV \(\sqrt{\frac{1}{4} - \frac{1}{9}} = 1.89 \text{ eV (656 nm)}\) well within the visible range, we can produce the essentially cylindrical field profile near the nanogap using common transition metals. In Figure 1D, the \(yz\) cross section of the overlap integrand \(\psi_{320} H_{\text{int}}^{(2)} \psi_{200}\) is shown in a 2 nm by 2 nm area with the hydrogen nucleus at \((x_o, z_o) = (3 \text{ nm}, 3 \text{ nm})\). The integrand \(\psi_{320} H_{\text{int}}^{(2)} \psi_{200}\) stays mostly positive, because the symmetries of \(z'^2 - x'^2\) from the Hamiltonian and \(2z'^2 - x'^2\) from \(\psi_{320}\) are quite similar. This result suggests that there will be a significant transition matrix element between 2S and 3D states, especially at the vicinity of the gap.

Note that \(\psi_{322} = \psi_{322} + \psi_{22}\) also couples to \(\psi_{200}\) through \(z'^2 - x'^2\), with a matrix element smaller by a factor \(\sqrt{3}\), whereas the \(-ex'z'z' \frac{\partial E_z}{\partial x} \bigg|_{(x_o, z_o)}\) part of the Hamiltonian does not participate significantly along the \(x = z\) line since \(\frac{\partial E_z}{\partial x} = 0\) along this line. Clearly, for general directions we also need to consider excitations into \(\psi_{321}\) and \(\psi_{322}\) through \(x'z'\).

To quantify how strong the forbidden transition matrix elements are between 2S and 3D states, we recall transition dipole moments of allowed excitations. Choosing a local electric field orientation as the \(z\) direction, a relevant dipole moment is defined as

\[
d_{\text{allowed}} = \frac{\langle \psi_{2s} | H_{\text{int}} | \psi_{3d} \rangle}{E_0} = \frac{\langle \psi_f | E_0 z | \psi_i \rangle}{E_0} = \frac{\langle \psi_f | e E_0 z | \psi_i \rangle}{E_0} - ea_n, \tag{5}
\]

where \(E_0\) is the electric field strength at the hydrogen nucleus and \(a_n\) is the Bohr radius. Analogously, we define the transition dipole moment of a forbidden 2S to 3D excitation such that

\[
d_{200 \rightarrow 320} = \frac{\langle \psi_{320} | H_{\text{int}} | \psi_{200} \rangle}{E_0(x_o, z_o)}. \tag{6}
\]

In Figure 2, we quantify forbidden dipole moments of the 2S to 3D transitions. We calculate the total forbidden dipole/transititon moment \(d_{2S \rightarrow 3D} = \sum_{n} d_{200 \rightarrow 32n}\) along the \(x = z\) line, as shown in Figure 2A. Calculations using the full \(H_{\text{int}}\) are represented by blue squares, while those using only \(H_{\text{int}}^{(2)}\) are represented by a blue line, displaying near perfect agreement. Finally, taking advantage of

\[
\frac{\partial E_z}{\partial z} = 1 \quad \text{and} \quad \frac{\partial E_z}{\partial x} = 0 \quad \text{along this line, we reach the}
\]

\[
E(x, z) = \left| k \right| \tag{7}
\]
A simple closed form approximation for the total forbidden dipole moment:

\[
\begin{align*}
    d_{2S \rightarrow 3D} &= \frac{2^{11/3} e a_B^2}{5^3 \sqrt{2 \pi x_0^3}} = 13.6 ea_B \frac{d_B}{\rho_o}, \\
    &= 0.95, \quad \text{from the origin} \rho_o \text{ are in nanometers. All three results agree rather well.}
\end{align*}
\]

To see the angular dependences of various forbidden excitations, we plot \( \sqrt{d_{200-320}^2 + d_{200-322}^2} \) in Figure 2B, demonstrating that indeed excitations into \( \psi_{320} \) and \( \psi_{322} \) are maximum along the \( x = z \) line. Transition dipole moments into \( \psi_{321} = \psi_{321}^{+} + \psi_{321}^{-} \), \( d_{200-321} \) are plotted in Figure 2C, showing an almost orthogonal angle dependence from that of \( \sqrt{d_{200-320}^2 + d_{200-322}^2} \). Adding all the forbidden dipoles, an almost isotropic
is obtained (Figure 2D), fitted rather well with the simple
analytical expression of \( \frac{0.719}{\rho_o} \) now applicable to all
directions within an error of 0.2–2%, as we move away
from the z-axis towards the x-axis.

We now study the width dependence of the forbidden
transitions. Since the cylindrical symmetry of the total for-
bidden dipole moment is only approximate in our geom-
etry, we expect to find deviations as we increase the gap
width. Figure 3A depicts the case of \( d_{2S \rightarrow 3D} \) for \( w = 3 \) nm.
Away from the gap, the cylindrical symmetry is recov-
ered, whereas for distances less than 5 nm, angular devia-
tions and weaker moments are evident. For \( w = 10 \) nm in
Figure 3B, the deviations are more pronounced, but again,
at distances larger than 10 nm, the forbidden dipole
moment converges to those of narrower gaps. Figure 3C
plots the forbidden dipole moment along the z-axis for
several gap widths. For gap widths of 3, 5, and 10 nm, the
forbidden dipole moments eventually converge to the \( 1/z \)
line at \( z \sim w \). Scanning along the x-direction for a fixed
\( z = 1 \) nm, the behavior is very different. At \( x = 0 \), forbid-
den dipole moments are smaller mainly because along
the middle of the gap, field curvatures are less. For \( w = 3, 5, \) and 10 nm, \( d_{2S \rightarrow 3D} \) peaks at \( x = \frac{w}{2} \) because sharp edges
of the charge distributions are located at \( \left( x = \frac{w}{2}, z = 0 \right) \).
Again, at all instances \( d_{2S \rightarrow 3D} \) recovers the \( \frac{0.719}{\rho_o} \) depend-
ence for \( x > 10 \) nm.

We now consider the excited state wavefunction

\[
\psi_{ex} \propto \left| \psi_{121} \right| \langle \psi_{121} | H_{int} | \psi_{200} \rangle + \left| \psi_{320} \right| \langle \psi_{320} | H_{int} | \psi_{200} \rangle \\
+ \left| \psi_{132} \right| \langle \psi_{132} | H_{int} | \psi_{200} \rangle
\]  

(6)

at various locations and conditions. The near-perfect
cylindrical symmetry of \( d_{2S \rightarrow 3D} \) for the 1 nm gap case sug-
gests a strong symmetry for \( \psi_{ex} \) as well. Figure 4A displays
the excited state wavefunction squared using the
full interaction Hamiltonian at three different locations.

![Figure 3](image-url)

**Figure 3:** Total forbidden dipole moment \( d_{2S \rightarrow 3D} \) plotted (A) when \( w = 3 \) nm and (B) when \( w = 10 \) nm. (C) Total forbidden dipole moment along
the z-axis when \( w = 1, 3, 5, \) and 10 nm. (Inset: a log-log plot). (D) Total forbidden dipole moment when the observation is along the x-axis
keeping \( z = 1 \) nm for \( w = 1, 3, 5, \) and 10 nm.
The excited state wavefunctions faithfully reproduce a pure $|\psi_{321}\rangle$ state within a coordinate system defined by the local field orientation. While physically intuitive, mathematically it is because \( \frac{(x^2-z^2)}{2} \frac{\partial E_x}{\partial z} - \frac{xz}{2} \frac{\partial E_x}{\partial x} \) when using the field profile of Eq. (2). We found that even with larger gap widths, excited wavefunctions’ orientations following the local field orientation remain largely unaffected except for right above the sharp edge (Figure 4B). In stark contrast, as shown in Figure 4C, the single wire case described by Eq. (1) displays wavefunctions not rotating with the local field orientation in a simplistic way. In spite of this complication, the excited wavefunctions remain a pure $|\psi_{321}\rangle$ state at a properly rotated coordinate system, which directly follows from the Hamiltonian of Eq. (4) containing only two quadratic terms: $(x^2-z^2); 2xz$. Replacing our source by a simple point dipole and using Eq. (6) with three-dimensional Hamiltonian produce a whole combination of D wavefunctions evident in Figure 4D. On the equator relative to the dipole orientation, pure $|\psi_{321}\rangle$ still get excited, whereas at most of other directions, all three states contribute.

4 Discussion and conclusion

With the 2S to 3D transition being essentially allowed near the gap, we estimate the spontaneous decay lifetime from
3D to 2S states. An effective dipole moment of one Bohr radius gives rise to a lifetime of 44 ns, six orders of magnitudes faster than the quadrupole transition in the vacuum. The physics of this spontaneous emission modification by nanostructures [27, 28] is clear in our case: in vacuum, the quadrupole transition is weaker than the dipole transition by $\sim \left(\frac{2\pi a_B}{\rho}\right)^2$, where $\lambda_0$ is the wavelength of light; on the other hand, near the nanogap with a distance of $\rho$, we replace this factor by $\sim \left(\frac{2\pi a_B}{\rho}\right)^2$, resulting in fast lifetimes comparable to those of the allowed transitions. Our infinite nanogaps have the advantage over point gaps in that it stretches to millimeter to centimeter length scale in the $y$-axis [11, 12], offering more robustness and million times larger effective areas than point gaps [29]. In attempts to break selection rules by going to shorter wavelength light, for example, X-rays [30], the transitions necessarily involve core orbitals of comparable short length scale, so that the effect is less dramatic than that presented here. Finally, while our technique applies to any S to D transitions, it may not apply to IS to 3S transitions such as described in [31]. This is because the quadratic potential still gives rise to zero matrix element between two S states because of symmetry.

Our two-dimensional quadratic potentials have, in addition to the obviously larger volume, another advantage over point source dipoles that also give rise to forbidden transitions in surface-enhanced Raman scattering and infrared absorption [23–26] in molecules. The excited wavefunctions are all of one nature, as shown in Figure 4A–C, which can give rise to constructive interference of quadrupole radiations. Finally, while an analytical field profile has been used throughout our paper, a COMSOL calculation assuming a 1 nm gap sandwiched by aluminum layers of 100 nm thickness at 656 nm produces a field profile of a cylindrical symmetry well described by Eq. (2). Finite-difference-time-domain calculations as well as vector field mapping experiments also support this picture [5, 32–34]. We therefore expect similar quantum mechanical results under finite elements electromagnetic simulations.

In conclusion, we have shown that the 2S-3D forbidden transition is allowed for all practical purposes, near the vicinity of a metallic nanogap. The relevant scale of this quadrupole transition becomes not the wavelength of light but the gap width and the distance of the atom from the gap. With million times larger effective volume than point gaps, together with the highly symmetric excited state wavefunctions, we foresee an intimate interaction between atomic spectroscopy and now mature nanogap technology in the near future, especially with free standing gaps. With the advantage of metallic nanogaps of infinite length with an ultimate field enhancement [32] whereby electromagnetic waves from microwaves to ultraviolet have all the same near-field profile [33, 34], up to the plasma frequency of metal, selection rule-free spectroscopy of atoms, molecules, and quantum dots will become of wide use.

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP: NRF-2015R1A3A2031768) (MOE: BK21 Plus Program-21A2013111123). DSK acknowledges COMSOL simulations of Taehee Kang and helpful discussions with professors Do-Young Noh, Yongil Shin, Changyoung Kim, and Jae-Hoon Park.

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