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Surface Electromagnetic Radiation from a Spatially Modulated Oscillating Dipole Layer

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Abstract. We present the calculation of surface electromagnetic radiation to all orders from a spatially modulated, oscillating dipole layer sandwiched between two dielectric media. The results properly include the macroscopic local field factors. In specular reflection direction, we show that the total radiation is partitioned into a term which is the zeroth-order counterpart to the higher-order diffraction and a term related only to the properties of two adjoining bulk media. The results unify the calculations by Shen and Heinz and McIntyre [1, 6, 7]

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Electromagnetic radiation from a surface with adsorbates have been a subject of extensive studies. Linear optical transmission and reflectance and optical sum-frequency generations are now widely exploited in studies of surface and interface properties [1–7]. Recently, a number of groups reported the detection of optical diffraction from monolayer adsorbate coverage gratings [8–11]. The optical diffraction have subsequently been exploited in studies of surface diffusion of adsorbates [12–14]. The theories of electromagnetic radiation from a surface region whose dimension is small compared to optical wavelengths are grouped into two types. In surface reflectance studies, it is conventional to treat the surface region as a macroscopic layer with an effective dielectric constant ε_m sandwiched between two bulk media with ε_1 and ε_2 [1–5]. The specularly reflected and transmitted radiation fields are evaluated with a classical stratified-layer model and the results can be found in literature [1–5]. In the studies of surface optical second-harmonic generation and optical diffraction from adsorbate coverage gratings, because there is no incident electromagnetic field varying with the same spatial and temporal phase factor, the radiation from the surface region is obtained by treating the latter as an oscillating dipole sheet and by integrating the dipole radiation over the sheet [6, 7, 10, 11]. The final results should properly include the effect of multiple reflection or the macroscopic local field factors.

There are two issues which remain to be fully addressed. The first is the proper macroscopic local field factors associated with higher-order linear diffraction. This has not been addressed clearly previously [11]. The second concerns how a linear differential reflectance in specular reflection is related to the higher-order diffraction. This further leads to the question of whether it is possible to deduce an adsorbate coverage grating profile with a linear optical diffraction measurement. In the case of optical second-harmonic diffraction, the specular and the higher-order diffraction fields are fairly simply related to the corresponding spatial Fourier components of an adsorbate coverage grating and were hence successfully used to determine the profile of such a grating [9]. In linear diffraction, however, this is not readily possible as the specularly reflected radiation from a coverage grating is accompanied by the bulk reflection [11].

In this paper, we plan to show that by arranging the Maxwell equations in a spatially modulated, oscillating dipole layer, the local field factors for all orders of optical diffraction can be obtained in a unfied way [10, 11]. Furthermore, the specular reflectance obtained with the classical stratified-layer model is partitioned into two parts: one is the zeroth-order counterpart to the higher-order diffraction, the other comes from the interface of the two adjoining media in the absence of adsorbates. We also show that, to a good approximation, the differential reflectance and the higher-order linear diffraction can be used to extract the profile of an adsorbate coverage grating.

1 A Spatially Modulated, Oscillating Dipole Layer and the Maxwell Equation

We define a surface layer, relevant to the studies of adsorbates on solids or liquids, to be the region which has a different optical response from those of the two adjoining bulk dielectric media. Usually, such a layer has a width d (a few Å) much smaller than optical wavelengths (10^4 Å). For metals and semiconductors, surface layers exist even without adsorbates [1]. We denote the susceptibility of a surface layer without adsorbates by χ_{m0}, and that with a

full monolayer of adsorbates by χ_m. At a finite coverage θ and in the limit that adsorbate-adsorbate interaction can be neglected, the susceptibility of the surface layer is given by

$$\chi_m(\theta) = \chi_{m0} + (\chi_m - \chi_{m0})\theta . \tag{1}$$

The linear dielectric constant of the surface layer is written as

$$\varepsilon_m(\theta) = 1 + 4\pi\chi_m(\theta) = \varepsilon_m(0) + 4\pi(\chi_m - \chi_{m0})\theta . \tag{2}$$

For adsorbates at the interface between an insulating solid and a gas or liquid phase medium, one may approximate χ_{m0} by that of the gas or liquid, and χ_m by that of the solid-phase adsorbates.

Let the surface layer be sandwiched between two bulk dielectric media with ε_1 and ε_2 and be irradiated with an external electromagnetic field $\mathbf{E}_{\text{inc}}(\mathbf{x}, t) = \mathbf{E}_{\text{inc}} \exp[\mathrm{i}(\mathbf{k}_{\text{inc}} \cdot \mathbf{x} - \omega t)]$ which is incident from the medium ε_1. The surface layer contains the x-y plane of the coordinate system and the z-axis is chosen to be along the surface normal and pointing from the medium ε_1 to the medium ε_2. We shall assume that $\mathbf{k}_{\text{inc}} = \hat{\mathbf{x}} k_{\text{inc},x} + \hat{\mathbf{z}} k_{\text{inc},z}$ and $|\mathbf{k}_{\text{inc}}|^2 = \varepsilon_1(\omega/c)^2$. The linear response of the surface layer is described by an oscillating dipole density,

$$\mathbf{P} = \chi_m(\theta)\mathbf{E} . \tag{3}$$

We note here that only the local response is considered here. The nonlocal corrections, which can be very important, are not included in the present formalism. The Maxwell equation for the electric field $\mathbf{E}$ in the surface layer is expressed as

$$[\nabla^2 + (\omega/c)^2]\mathbf{E} = -4\pi(\omega/c)^2\mathbf{P} . \tag{4}$$

If the adsorbate coverage θ varies periodically in x-direction along the surface with a period $2a$,

$$\theta = \sum_{n=-\infty}^{+\infty} \theta_n \exp(\mathrm{i}n\pi x/a) \tag{5}$$

(here we assume $\theta_n = \theta_{-n}$), the resultant polarization $\mathbf{P}$ prescribes a spatially modulated, oscillating dipole layer [11]. To calculate the linear diffraction, we decompose $\mathbf{E}$ into a Fourier series,

$$\mathbf{E} = \sum_{n=-\infty}^{+\infty} \mathbf{E}_n , \qquad \mathbf{E}_n \propto \exp[\mathrm{i}(k_{\text{inc},x} + n\pi/a)x] . \tag{6}$$

Substituting (3, 5, 6) into (4), and separating different spatial Fourier components, we arrive at an equation for the n-th order electric field in the surface layer,

$$[\nabla^2 + \varepsilon_m(\theta_0)(\omega/c)^2]\mathbf{E}_n = -4\pi(\omega/c)^2(\chi_m - \chi_{m0}) \sum_{n' \neq n} \theta_{n-n'}\mathbf{E}_{n'} \exp[(\mathrm{i}(n-n')\pi x/a] . \tag{7}$$

Normally, this is a set of coupled equations. For our purpose, we shall assume that the Fourier coefficient θ_n decreases rapidly with n.

For the zeroth-order radiation, the leading contribution from the surface layer is already included in $\varepsilon_m(\theta_0)$ on the left-hand side of (7) and we have

$$[\nabla^2 + \varepsilon_m(\theta_0)(\omega/c)^2]\mathbf{E}_0 = 0 . \tag{8}$$

For the higher-order radiation with $n \geq 1$, only the term containing $\mathbf{E}_0$ on the left-hand side of (7) needs to be kept,

$$[\nabla^2 + \varepsilon_m(\theta_0)(\omega/c)^2]\mathbf{E}_n = -4\pi(\omega/c)^2(\chi_m - \chi_{m0})\theta_n\mathbf{E}_0 \exp(\mathrm{i}n\pi x/a) . \tag{9}$$

From these equations, we can discuss the surface electromagnetic radiation.

2 Higher-Order Diffraction with $n \geq 1$

As we stated earlier, since there is no incident electromagnetic field with the same spatial phase factor as that of a higher-order diffraction, the latter is conveniently obtained with the oscillating dipole sheet method of Shen and Heinz [6, 7]. The dipole density associated with the n-th-order diffraction

$$\mathbf{P}_n = (\chi_m - \chi_{m0})\theta_n\mathbf{E}_0 \exp(\mathrm{i}n\pi x/a) \tag{10}$$

is embedded in a polarizable medium with an effective dielectric constant $\varepsilon_m(\theta_0)$. From (10), we define a surface polarization density vector by integrating both sides over the thickness d of the surface layer,

$$\mathbf{P}_n^{\text{s}} = (\chi_m - \chi_{m0})d\theta_n\mathbf{E}_0 \exp(\mathrm{i}n\pi x/a) . \tag{11}$$

The radiation fields corresponding to the n-th-order diffraction in the medium ε_1 are easily obtained for both p- and *s-polarized* waves [6, 7]

$$E_{p,n} = \frac{\mathrm{i}2\pi k_1}{\varepsilon_1 k_{1n,z}}(k_{1n,z}L_{n,xx}P^{\text{s}}_{n,x} + k_{n,x}L_{n,zz}P^{\text{s}}_{n,z}) , \tag{12}$$

$$E_{s,n} = \frac{\mathrm{i}2\pi k_1^2}{\varepsilon_1 k_{1n,z}} L_{n,yy}P^{\text{s}}_{n,y} . \tag{13}$$

The local field factors for the n-th-order diffraction are given by:

$$L_{n,xx} = \frac{2\varepsilon_1 k_{2n,z}}{\varepsilon_2 k_{1n,z} + \varepsilon_1 k_{2n,z}} , \tag{14}$$

$$L_{n,zz} = \frac{2\varepsilon_1 k_{1n,z}}{\varepsilon_2 k_{1n,z} + \varepsilon_1 k_{2n,z}} \frac{\varepsilon_2}{\varepsilon_m(\theta_0)} , \tag{15}$$

$$L_{n,yy} = \frac{2k_{1n,z}}{k_{1n,z} + k_{2n,z}} , \tag{16}$$

where

$$k_{1n,z} = +\sqrt{k_1^2 - (k_{\text{inc},x} + n\pi/a)^2} ,$$
$$k_{2n,z} = +\sqrt{k_2^2 - (k_{\text{inc},x} + n\pi/a)^2} , \tag{17}$$
$$k_{n,x} = k_{\text{inc},x} + n\pi/a .$$

$k_{1,2}^2$ are given by $\varepsilon_{1,2}(\omega/c)^2$. The zeroth-order electric field $\mathbf{E}_0$ in the surface layer is obtained by the usual stratified-layer calculation [1–5]. It is related to the incident field $\mathbf{E}_{\text{inc}}$ by the local field factors given by (14–16) with $n = 0$.

These results are readily extended to optical second-harmonic diffraction [6, 7, 10]. In those cases, the linear responses of the surface layer to the incident fundamental field and the outgoing second-harmonic field are included in the local field factors (14–16). For the oscillating polarization density at second-harmonics, one replaces the

linear susceptibility $\chi_m - \chi_{m0}$ on the right-hand sides of (10) and (11) with the second-harmonic susceptibility $\chi_m^{(2)} - \chi_{m0}^{(2)}$.

3 The Zeroth-Order Radiation from the Surface Layer

The specularly reflected electric field consists of one part from an ideally abrupt interface of ε_1 and ε_2 and another part from the surface layer. The contribution from the surface layer is further separated into one from the unperturbed surface region with $\varepsilon_m(0)$ and one proportional to $(\chi_m - \chi_{m0})\theta_0$. The latter is the zeroth-order counterpart of the higher-order diffraction. To see it clearly, we partition the electric field $\mathbf{E}_0$ into two: $\mathbf{E}_{00}$ which is independent of adsorbates and satisfies

$$[\nabla^2 + \varepsilon_m(0)(\omega/c)^2]\mathbf{E}_{00} = 0\,, \tag{18}$$

and $\mathbf{E}_{01}$ which is linearly dependent upon the mean coverage θ_0 of the adsorbates,

$$[\nabla^2 + \varepsilon_m(\theta_0)(\omega/c)^2]\mathbf{E}_{01} = -4\pi(\omega/c)^2(\chi_m - \chi_{m0})\theta_0\mathbf{E}_{00}\,. \tag{19}$$

Equation (18) or $\mathbf{E}_{00}$ is solved with the incident field $\mathbf{E}_{\text{inc}}$ in the medium ε_1. $\mathbf{E}_{00}$ is thus related to $\mathbf{E}_{\text{inc}}$ by a slightly different set of local field factors which are obtained by replacing $\varepsilon_m(\theta_0)$ with $\varepsilon_m(0)$ in (14–16). Equation (19) is solved without any incident field and thus has the same form as (9) for the higher-order diffraction except that $\mathbf{E}_0$ is replaced with $\mathbf{E}_{00}$. The sum of the reflected radiation fields associated with $\mathbf{E}_{00}$ and $\mathbf{E}_{01}$ gives the result of the usual surface reflectance calculation [1–5]. We note that for *s-polarized* radiation, $\mathbf{E}_0 = \mathbf{E}_{00}$. Hence the specularly reflected, *s-polarized* radiation field $\mathbf{E}_{s,0}$ associated with $\mathbf{E}_{01}$ is the zeroth-order counterpart of the higher-order diffraction and is given by (13) with $n = 0$. The ratio of $\mathbf{E}_{s,0}/\mathbf{E}_{s,n}$ is proportional to θ_0/θ_n. Thus if $\mathbf{E}_{s,0}$ can be deduced, together with higher-order diffraction, one can reconstruct the profile of a spatially modulated dipole density [9].

Unfortunately, the total specularly reflected field is the sum of the unperturbed reflected field $\mathbf{E}_{s0}$ determined by (18) and $\mathbf{E}_{s,0}$. In a differential reflectance experiment, one measures $|\mathbf{E}_{s0} + \mathbf{E}_{s,0}|^2 - |\mathbf{E}_{s0}|^2$ or $\Delta R = R - R_0$. The intensity $I_{s,0}$ corresponding to $\mathbf{E}_{s,0}$ may only be expressed as

$$I_{s,0} = \frac{\Delta R^2}{4R_0[\cos(\Theta_{s,0} - \Theta_{s0})]^2} \propto \theta_0^2\,. \tag{20}$$

$\Theta_{s,0}$ and Θ_{s0} are the phase angles for $\mathbf{E}_{s,0}$ and $\mathbf{E}_{s0}$. They usually are not known *a priori* [1–5].

We now explore whether $I_{s,0}$ may be determined accurately enough from ΔR and R_0 such that one may deduce the profile of a coverage grating from the ratio of $I_{s,0}/I_{s,n}$. In the case of optical second-harmonic diffraction, the strength of the specularly reflected radiation field generated from the two bulk media possessing inversion centers are suppressed by a factor of 10^3 to 10^4 [9]. Consequently, the radiation from a surface layer becomes comparable in strength to that from the abrupt interface of the two bulk media. This enabled Zhu and Shen to calibrate the specularly reflected optical Second-Harmonic Generation (SHG) as a function of the mean coverage of CO on Ni(111). From the calibration and the measurement of higher-order diffraction and the specular reflected SHG, they were able to determine the spatial Fourier components of a CO coverage grating and to reconstruct the profile [9]. Unfortunately, the same calibration can not be easily and reliably performed in a linear reflectance measurement. This is because the field strength of the bulk reflection $\mathbf{E}_{s0}$ is no longer suppressed by the crystal symmetry and is a factor of 10^3 stronger than the field $\mathbf{E}_{s,0}$ generated from the surface layer alone.

For practical purposes, however, one may simply take $\cos(\Theta_{s,0} - \Theta_{s0}) \approx 1$, so that

$$I_{s,0} = \frac{\Delta R^2}{4R_0}\,. \tag{21}$$

One may also obtain the phase-angle factor $\cos(\Theta_{s,0} - \Theta_{s0})$ approximately by assuming that the surface layer consists of one atomic layer of a thickness d whose optical response is changed from that of the bulk metal to an insulator by adsorbates. The bulk region which contributes to R_0 has an effective thickness given by $(1/2)|k_{2,0,z}|$ [6, 7]. The maximum differential reflectance is then roughly given by

$$\Delta R_{\max} = 4\sqrt{R_0}|k_{2,0,z}d|\cos(\Theta_{s,0} - \Theta_{s0})\,. \tag{22}$$

Combining (20) and (22), we arrive at

$$I_{s,0} = 4|k_{2,0,z}d|^2\theta_0^2\,. \tag{23}$$

Both (21) and (23) can give an estimate of θ_0 which is directly related to the higher-order Fourier components θ_n. They can be in turn used to give a reasonable estimate of a coverage grating profile.

4 Conclusion

We have shown that the radiation fields reflected from a spatially modulated, oscillating dipole layer can be treated in a unified way. The macroscopic local field factors for the higher-order diffraction are presented. We have identified the term in specular direction which is the zeroth-order counterpart of the higher-order diffraction. It can be estimated from a differential reflectance measurement such that the profile of a spatially modulated, oscillating dipole density may also be reconstructed in a linear optical diffraction experiment.

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