• In situ EXAFS studies

- In situ EXAFS studies
- Angle Resolved Photoemission

- In situ EXAFS studies
- Angle Resolved Photoemission
- Resonant Scattering

- In situ EXAFS studies
- Angle Resolved Photoemission
- Resonant Scattering
- Friedel's Law

- In situ EXAFS studies
- Angle Resolved Photoemission
- Resonant Scattering
- Friedel's Law
- Bijvoet (Bay-voot) Pairs

Homework Assignment #7: Chapter 7: 2, 3, 9, 10, 11 due Tuesday, April 23, 2015

- In situ EXAFS studies
- Angle Resolved Photoemission
- Resonant Scattering
- Friedel's Law
- Bijvoet (Bay-voot) Pairs
- MAD Phasing

Homework Assignment #7: Chapter 7: 2, 3, 9, 10, 11 due Tuesday, April 23, 2015

- In situ EXAFS studies
- Angle Resolved Photoemission
- Resonant Scattering
- Friedel's Law
- Bijvoet (Bay-voot) Pairs
- MAD Phasing
- Quantum Origin of Resonant Scattering

Homework Assignment #7: Chapter 7: 2, 3, 9, 10, 11 due Tuesday, April 23, 2015

# Mark I operando fuel cell



R. Viswanathan et al., "In-situ XANES study of carbon supported Pt-Ru anode electrocatalysts for reformate-air polymer electrolyte fuel cells", *J. Phys. Chem.* **B 106**, 3458 (2002).

- Transmission mode
- <1 mm of graphite
- Pt/Ru on anode
- Pd on cathode
- 35°C operating temp
- 1-2 min scan time



# Mark II operando fuel cell



E.A. Lewis et al., "Operando x-ray absorption and infrared fuel cell spectroscopy", *Electrochim. Acta.* **56**, 8827 (2011).

- Air-breathing cathode
- Pd on anode
- $1.2 \text{ mg/cm}^2$  loading
- 50°C operating temp
- Pt L<sub>3</sub> and Ni K edges
- Continuous scan mode @ mrcat



# Oxygen reduction at a PtNi cathode



Anode: 0 V vs. SHE  $2 H_2 \longrightarrow 4 H^+ + 4 e^-$ Cathode: 1.23 V s. SHE  $O_2 + 4 H^+ + 4 e^- \longrightarrow 2 H_2 O$ 

breaking  $O\!-\!O$  bond is the rate limiting step

U.S. Department of Defense (DoD) Fuel Cell Test and Evaluation Center (FCTec)



## Fuel cell performance and open questions



PtNi/Pd has higher open circuit voltage, similar performance to Pt/Pd.

## Fuel cell performance and open questions



PtNi/Pd has higher open circuit voltage, similar performance to Pt/Pd.

Pt: How do reactants adsorb on platinum surface?

- Do all faces of Pt adsorb equally well?
- Is there a change in location with coverage?

PtNi: Why is ORR improved with bimetallic catalyst?

- Pt electronic structure modified
- Pt catalyst geometric structure modified
- Static oxygen adsorbates inhibited
- Overpotential reduced

How do real catalysts differ from model systems?

PHYS 570 - Spring 2015

# Pt/C and PtNi/C comparison



Attempt to get global information about the oxygen

Fit all potentials with same metal core parameters for each catalyst

Simultaneous fit of Pt and Ni edges in  $\ensuremath{\text{PtNi/C}}$  with constraint on Pt-Ni distance

Fit in k,  $k^2$ , and  $k^3$  weighting simultaneously

M-O path constraints

- length common across potentials
- $\sigma^2$  fixed to 0.01
- Pt-O in PtNi/C are refined with a single occupation #

# Example fits



### Fit results

	Pt/C	PtNi/C			
		Pt		Ni	
N <sub>Pt</sub>	$8.7\pm0.2$	N <sub>Pt</sub>	$6.1\pm0.3$	N <sub>Ni</sub>	$3.7\pm0.2$
R <sub>Pt-Pt</sub>	$2.749\pm0.001$	R <sub>Pt-Pt</sub>	$2.692\pm0.003$	R <sub>Ni-Ni</sub>	$2.572\pm0.006$
		N <sub>Ni</sub>	$3.4\pm 0.1$	N <sub>Pt</sub>	$8.9\pm 0.5$
			R <sub>Pt-Ni</sub>	$2.635\pm0.004$	
		N <sub>Total</sub>	$9.5\pm0.4$	N <sub>Total</sub>	$12.6\pm0.7$
R <sub>Pt-O</sub>	$2.02\pm0.01$	R <sub>Pt-O</sub>	$2.09\pm0.03$	R <sub>Ni-O</sub>	$1.90\pm0.01$

Note the Pt-Pt and Pt-O bond lengths as well as total metal near neighbors

C. Segre (IIT)

PHYS 570 - Spring 2015

### What does Ni really do?

Resides predominantly in metal core of nanoparticle Eliminates static Pt-O bonds at all potentials Number of O near neighbors "increases" with potential Lengthens Pt-O and shortens Pt-Pt bond Reduces Pt white line in most reduced state (0 mV) Open circuit voltage is increased (reduction in overpotential)

Can we use modeling to establish specific mechanism?

- Pt-Pt bond reduction (weakening of Pt-O bond)?
- Electron donation to Pt d-band (weakening of Pt-O bond)?
- Stronger affinity for oxygen?

### Pt cluster modeling

By using FEFF8.4, which performs full multiple-scattering self-consistent calculations, we can explore the implications of the "ligand effect" and the "strain effect" on the electronic state of Pt.



Separate the effects of

- (a) Shorter Pt-Pt distance
- (b) charge transfer from subsurface Ni

Use experimentally determined distances

Calculate local density of states

Calculate XANES spectrum

Q. Jia, et al., "Structure-property-activity correlations of Pt-bimetallic nanoparticles: a theoretical study" *Electrochimica Acta* bf 88, 604 (2013).

### Cluster calculation results

Strain effect: shorter Pt-Pt bond  $\rightarrow$  broader and lower Pt d-band

- serves to weaken the Pt-O bond
- White line at absorption edge is reduced
- In agreement with DFT calculations (Nørskov et al.)

Ligand effect: subsurface Ni  $\rightarrow$  sharpens and raises Pt d-band

- Raises chemisorption energy
- Increases white line

Net effect dominated by strain effect

Predictive ability

- Moving down periodic table (Ru, Ag)
- Moving left across periodic table (towards Mn)

# Methanol oxidation by a PtRu anode



Anode: 0.02 V vs. SHE  $CH_3OH + H_2O \longrightarrow 6H + CO_2 + 6e^-$ 

Cathode: 1.23 V s. SHE $\frac{3}{2} \text{ O}_2 + 6 \text{ H}^+ + 6 \text{ e}^- - 3 \text{ H}_2 \text{ O}$ 

Pt surface poisoned by CO

U.S. Department of Defense (DoD) Fuel Cell Test and Evaluation Center (FCTec)

The presence of Ru promotes CO oxidation through a "bi-functional mechanism"

$$Pt-(CO)_{ads} + Ru-OH \longrightarrow Pt + RuCO_2 + H^+ + 2e^-$$

C. Segre (IIT)

PHYS 570 - Spring 2015

# Ru EXAFS fitting



- Addition of Ru-O/C neighbors improves the EXAFS fit
- The peak at about 1.3 Å is ascribed to oxygen bound to Ru
- The asymmetric distribution of the Ru-O/C peak is consistent with disorder

PHYS 570 - Spring 2015

#### Metal nanoparticle structure

- First shell analysis
- Fit Pt and Ru EXAFS simultaneously at each potential. No potential dependence observed
- Simultaneously fit Pt and Ru data at all potentials. Identical overall average coordination was observed
- Use fractional coordination numbers, x (Pt around Ru) and y (Ru around Pt) and total coordination number about each atom, N
- Bond lengths and Debye-Waller factors are consistent with literature values for C supported Pt-Ru catalyst (Russel 2001, Camara 2002)

$$\begin{array}{ccc} N & 8.2 \pm 0.2 \\ x & 0.54 \pm 0.02 \\ y & 0.27 \pm 0.02 \end{array} \qquad \qquad \frac{[Ru]}{[Pt]} = \frac{y}{x} = 0.50 \end{array}$$

### Metal core restucturing

As-received catalyst Ru oxidation ~ 58 % N = 5.6  $\frac{[Ru]}{[Pt]} = \frac{y}{x} = 0.44$ Pt-O bonds present # Ru-O bonds ~2.8 In-situ catalyst Ru oxidation  $\sim 15$  % N = 8.2 $\frac{[Ru]}{[Pt]} = \frac{y}{x} = 0.50$ No Pt-O bonds # Ru-O/C bonds  $\sim 0.24$ 

- Inner core has more Pt than Ru
- Ru on surface and outside of metallic nanoparticle

S. Stoupin, et al., "Pt and Ru X-ray absorption spectroscopy of PtRu anode catalysts in operating direct methanol fuel cells" *J. Phys. Chem.* **110**, 9932 (2006).

C. Segre (IIT)

PHYS 570 - Spring 2015

### Role of Ru in CO oxidation?

- PtRu bifunctional catalyst improves performance
- In commercial PtRu catalysts there is always a lot of inactive Ru-oxide (?)
- Ru signal dominated by metallic Ru environment
- How does Ru behave in the presence of reactants adsorbed on platinum surface?

Core-shell nanoparticles can resolve these questions

#### Ru-decorated Pt nanoparticles









C. Segre (IIT)

### Electrochemical performance



Without Methanol Low V peaks are H<sup>+</sup> stripping Dip at  $\sim 0.5$  V is oxygen stripping Ru shifts potential on all peaks

### Electrochemical performance



Without Methanol Low V peaks are H<sup>+</sup> stripping Dip at  $\sim 0.5$  V is oxygen stripping Ru shifts potential on all peaks

#### With Methanol

Continual current growth is due to methanol oxidation

Ru improves current by removing the CO which blocks active sites

# Ru EXAFS



## Ru EXAFS



### Ru-M paths



#### Without methanol

#### With methanol

### Ru-M paths



#### Without methanol

Ru-M distances are longer and  $RuO_2$  is formed at high potentials

#### With methanol

### Ru-M paths



#### Without methanol

Ru-M distances are longer and  $RuO_2$  is formed at high potentials

#### With methanol

Ru-M distances are shorter and remain the same at all potentials

# Ru-O/C paths



#### Without methanol

#### With methanol

# Ru-O/C paths



#### Without methanol

Above 375 mV Ru-O paths appear and total number of Ru-O neighbors increases to that of RuO<sub>2</sub>

#### With methanol

# Ru-O/C paths



#### Without methanol

Above 375 mV Ru-O paths appear and total number of Ru-O neighbors increases to that of RuO<sub>2</sub>

#### With methanol

Ru has one low Z neighbor at all potentials (carbon); a second above 175 mV (oxygen) with constant bond lengths and slightly increasing numbers
# **Bi-functional mechanism**



C. Pelliccione et al., "In situ Ru K-Edge x-ray absorption spectroscopy study of methanol oxidation mechanisms on model submonolayer Ru on Pt nanoparticle electrocatalyst" *J. Phys. Chem.* **C 117**, 18904 (2013).

C. Segre (IIT)

PHYS 570 - Spring 2015

# Synthesis of Sn-graphite nanocomposites



XRD shows a small amount of Sn metal in addition to  $Sn_3O_2(OH)_2$ 





### *In situ* battery box



Pouch cell clamped against front window in helium environment

C. Segre (IIT)

PHYS 570 - Spring 2015

### *In situ* battery box



Suitable for both transmission and fluorescence measurements

C. Segre (IIT)

PHYS 570 - Spring 2015





C. Segre (IIT)



Fresh electrode can be fit with  $Sn_3O_2(OH)_2$  structure which is dominated by the near neighbor Sn-O distances



Fresh electrode can be fit with  $Sn_3O_2(OH)_2$  structure which is dominated by the near neighbor Sn-O distances

Only a small amount of metallic Sn-Sn distances can be seen

C. Segre (IIT)



Reduction of number of Sn-O near neighbors and 3 Sn-Li paths characteristic of the  $\rm Li_{22}Sn_5$  structure



Metallic Sn-Sn distances appear but Sn-Li paths are still present, further reduction in Sn-O near neighbors.



C. Segre (IIT)



Number of Li near neighbors oscillates with the charge/discharge cycles but never returns to zero



Number of Li near neighbors oscillates with the charge/discharge cycles but never returns to zero

In situ cell promotes accelerated aging because of Sn swelling and the reduced pressure of the thin PEEK pouch cell assembly



C. Pelliccione, E.V. Timofeeva, and C.U. Segre, "In situ XAS study of the capacity fading mechanism in hybrid  $Sn_3O_2(OH)_2$ /graphite battery anode nanomaterials" *Chem. Mater.* **27**, 574-580 (2015).

Photoemission is the complement to XAFS. It probes the filled states below the Fermi level



Photoemission is the complement to XAFS. It probes the filled states below the Fermi level

The dispersion relation of electrons in a solid,  $\mathcal{E}(\vec{q})$  can be probed by angle resolved photoemission



Photoemission is the complement to XAFS. It probes the filled states below the Fermi level

The dispersion relation of electrons in a solid,  $\mathcal{E}(\vec{q})$  can be probed by angle resolved photoemission

$$\mathcal{E}_{kin}, \ \theta \ \longrightarrow \ \mathcal{E}(\vec{q})$$



Photoemission is the complement to XAFS. It probes the filled states below the Fermi level

The dispersion relation of electrons in a solid,  $\mathcal{E}(\vec{q})$  can be probed by angle resolved photoemission

$$\begin{aligned} \mathcal{E}_{kin}, \ \theta & \longrightarrow \ \mathcal{E}(\vec{q}) \\ \mathcal{E}_{kin} &= \frac{\hbar^2 q_v^2}{2m} = \hbar \omega - \phi - \mathcal{E}_B \\ \mathcal{E}_B &= \mathcal{E}_F - \mathcal{E}_i \end{aligned}$$



The electric field between the two hemispheres has a  $R^2$  dependence from the center of the hemispheres



The electric field between the two hemispheres has a  $R^2$  dependence from the center of the hemispheres

Electrons with  $\mathcal{E}_0$ , called the "pass energy", will follow a circular path of radius  $R_0 = (R_1 + R_2)/2$ 



The electric field between the two hemispheres has a  $R^2$  dependence from the center of the hemispheres

Electrons with  $\mathcal{E}_0$ , called the "pass energy", will follow a circular path of radius  $R_0 = (R_1 + R_2)/2$ 



The electric field between the two hemispheres has a  $R^2$  dependence from the center of the hemispheres

Electrons with  $\mathcal{E}_0$ , called the "pass energy", will follow a circular path of radius  $R_0 = (R_1 + R_2)/2$ 

Electrons with lower energy will fall inside this circular path while those with higher enegy will fall outside



Up to now, scattering has been treated classically and the result of radiation interaction with "free" electrons.

Up to now, scattering has been treated classically and the result of radiation interaction with "free" electrons.

This is not a good approximation since we know:

Up to now, scattering has been treated classically and the result of radiation interaction with "free" electrons.

This is not a good approximation since we know:

$$f(\vec{Q},\omega) = f^0(\vec{Q}) + f'(\omega) + if''(\omega)$$



Up to now, scattering has been treated classically and the result of radiation interaction with "free" electrons.

 $f(\vec{Q},\omega) = f^0(\vec{Q}) + f'(\omega) + if''(\omega)$ 

This is not a good approximation since we know:



The absorption cross section can be modeled as a sum of forced, dissipative oscillators with distribution  $g(\omega_s)$ .

Up to now, scattering has been treated classically and the result of radiation interaction with "free" electrons.

 $f(\vec{Q},\omega) = f^0(\vec{Q}) + f'(\omega) + if''(\omega)$ 

This is not a good approximation since we know:



The absorption cross section can be modeled as a sum of forced, dissipative oscillators with distribution  $g(\omega_s)$ .

Up to now, scattering has been treated classically and the result of radiation interaction with "free" electrons.

 $f(\vec{Q},\omega) = f^0(\vec{Q}) + f'(\omega) + if''(\omega)$ 

This is not a good approximation since we know:



The absorption cross section can be modeled as a sum of forced, dissipative oscillators with distribution  $g(\omega_s)$ .

This will produce the resonant scattering term but not the XANES and EXAFS, which are purely quantum effects.

Up to now, scattering has been treated classically and the result of radiation interaction with "free" electrons.

 $f(\vec{Q},\omega) = f^0(\vec{Q}) + f'(\omega) + if''(\omega)$ 

This is not a good approximation since we know:



Photon energy

The absorption cross section can be modeled as a sum of forced, dissipative oscillators with distribution  $g(\omega_s)$ .

This will produce the resonant scattering term but not the XANES and EXAFS, which are purely quantum effects

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

assuming a solution of the form

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

assuming a solution of the form

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

$$x = x_0 e^{-i\omega t}$$

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

assuming a solution of the form

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

$$x = x_0 e^{-i\omega t}$$
$$\dot{x} = -i\omega x_0 e^{-i\omega t}$$
Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

assuming a solution of the form

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

$$x = x_0 e^{-i\omega t}$$
$$\dot{x} = -i\omega x_0 e^{-i\omega t}$$
$$\ddot{x} = -\omega^2 x_0 e^{-i\omega t}$$

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

assuming a solution of the form

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

$$x = x_0 e^{-i\omega t}$$
$$\dot{x} = -i\omega x_0 e^{-i\omega t}$$
$$\ddot{x} = -\omega^2 x_0 e^{-i\omega t}$$

$$(-\omega^2 - i\omega\Gamma + \omega_s^2)x_0e^{-i\omega t} = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

assuming a solution of the form

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

$$x = x_0 e^{-i\omega t}$$
$$\dot{x} = -i\omega x_0 e^{-i\omega t}$$
$$\ddot{x} = -\omega^2 x_0 e^{-i\omega t}$$

$$(-\omega^{2} - i\omega\Gamma + \omega_{s}^{2})x_{0}e^{-i\omega t} = -\left(\frac{eE_{0}}{m}\right)e^{-i\omega t}$$
$$x_{0} = -\left(\frac{eE_{0}}{m}\right)\frac{1}{(\omega_{s}^{2} - \omega^{2} - i\omega\Gamma)}$$

Consider an electron under the influence of an oscillating electric field  $\vec{E}_{in} = \hat{x}E_0e^{-i\omega t}$ .

where  $\Gamma$  is the damping constant,  $\omega_s$  is the resonant frequency of the oscillator, and  $\Gamma \ll \omega_s$ .

assuming a solution of the form

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 x = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$

$$x = x_0 e^{-i\omega t}$$
$$\dot{x} = -i\omega x_0 e^{-i\omega t}$$
$$\ddot{x} = -\omega^2 x_0 e^{-i\omega t}$$

$$(-\omega^2 - i\omega\Gamma + \omega_s^2)x_0e^{-i\omega t} = -\left(\frac{eE_0}{m}\right)e^{-i\omega t}$$
  
 $x_0 = -\left(\frac{eE_0}{m}\right)\frac{1}{(\omega_s^2 - \omega^2 - i\omega\Gamma)}$ 

The amplitude of the response has a resonance and dissipation

PHYS 570 - Spring 2015

$$E_{rad}(R,t) = \left(rac{e}{4\pi\epsilon_0 Rc^2}
ight)\ddot{x}(t-R/c)$$

$$E_{rad}(R,t) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)\ddot{x}(t-R/c) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)(-\omega^2)x_0e^{-i\omega t}e^{i\omega R/c}$$

$$E_{rad}(R,t) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)\ddot{x}(t-R/c) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)(-\omega^2)x_0e^{-i\omega t}e^{i\omega R/c}$$
$$= \frac{\omega^2}{(\omega_s^2 - \omega^2 - i\omega\Gamma)}\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)E_0e^{-i\omega t}\left(\frac{e^{ikR}}{R}\right)$$

$$E_{rad}(R,t) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)\ddot{x}(t-R/c) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)(-\omega^2)x_0e^{-i\omega t}e^{i\omega R/c}$$
$$= \frac{\omega^2}{(\omega_s^2 - \omega^2 - i\omega\Gamma)}\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)E_0e^{-i\omega t}\left(\frac{e^{ikR}}{R}\right)$$
$$\frac{E_{rad}(R,t)}{E_{in}} = -r_0\frac{\omega^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}\left(\frac{e^{ikR}}{R}\right)$$

$$E_{rad}(R,t) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)\ddot{x}(t-R/c) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)(-\omega^2)x_0e^{-i\omega t}e^{i\omega R/c}$$
$$= \frac{\omega^2}{(\omega_s^2 - \omega^2 - i\omega\Gamma)}\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)E_0e^{-i\omega t}\left(\frac{e^{ikR}}{R}\right)$$
$$\frac{E_{rad}(R,t)}{E_{in}} = -r_0\frac{\omega^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}\left(\frac{e^{ikR}}{R}\right) = -r_0f_s\left(\frac{e^{ikR}}{R}\right)$$

The radiated (scattered) electric field at a distance R from the electron is directly proportional to the electron's acceleration with a retarded time t' = t - R/c (allowing for the travel time to the detector).

$$E_{rad}(R,t) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)\ddot{x}(t-R/c) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)(-\omega^2)x_0e^{-i\omega t}e^{i\omega R/c}$$
$$= \frac{\omega^2}{(\omega_s^2 - \omega^2 - i\omega\Gamma)}\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)E_0e^{-i\omega t}\left(\frac{e^{ikR}}{R}\right)$$
$$\frac{E_{rad}(R,t)}{E_{in}} = -r_0\frac{\omega^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}\left(\frac{e^{ikR}}{R}\right) = -r_0f_s\left(\frac{e^{ikR}}{R}\right)$$

which is an outgoing spherical wave with scattering amplitude

The radiated (scattered) electric field at a distance R from the electron is directly proportional to the electron's acceleration with a retarded time t' = t - R/c (allowing for the travel time to the detector).

$$E_{rad}(R,t) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)\ddot{x}(t-R/c) = \left(\frac{e}{4\pi\epsilon_0 Rc^2}\right)(-\omega^2)x_0e^{-i\omega t}e^{i\omega R/c}$$
$$= \frac{\omega^2}{(\omega_s^2 - \omega^2 - i\omega\Gamma)}\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)E_0e^{-i\omega t}\left(\frac{e^{ikR}}{R}\right)$$
$$\frac{E_{rad}(R,t)}{E_{in}} = -r_0\frac{\omega^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}\left(\frac{e^{ikR}}{R}\right) = -r_0f_s\left(\frac{e^{ikR}}{R}\right)$$

which is an outgoing spherical wave with scattering amplitude

$$f_s = \frac{\omega^2}{(\omega^2 + \omega_s^2 + i\omega\Gamma)}$$

The scattering factor can be rewritten

$$f_{s} = \frac{\omega^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_{s}$ 

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

$$\chi(\omega) = f'_s + i f''_s$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\chi(\omega) = f_{s}' + if_{s}'' = \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction whose real and imaginary components can be extracted

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\chi(\omega) = f_{s}' + if_{s}'' = \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction whose real and imaginary components can be extracted

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\chi(\omega) = f_{s}' + if_{s}'' = \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

$$\chi(\omega) = \frac{\omega_s^2}{(\omega^2 + \omega_s^2 + i\omega\Gamma)} \cdot \frac{(\omega^2 + \omega_s^2 - i\omega\Gamma)}{(\omega^2 + \omega_s^2 - i\omega\Gamma)}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction whose real and imaginary components can be extracted

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$(\omega) = f_{s}' + if_{s}'' = \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

$$\chi(\omega) = \frac{\omega_s^2}{(\omega^2 + \omega_s^2 + i\omega\Gamma)} \cdot \frac{(\omega^2 + \omega_s^2 - i\omega\Gamma)}{(\omega^2 + \omega_s^2 - i\omega\Gamma)} = \frac{\omega_s^2(\omega^2 + \omega_s^2 - i\omega\Gamma)}{(\omega^2 + \omega_s^2)^2 + (\omega\Gamma)^2}$$

 $\chi$ 

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction whose real and imaginary components can be extracted

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\chi(\omega) = f_{s}' + if_{s}'' = \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

$$\chi(\omega) = \frac{\omega_s^2}{(\omega^2 + \omega_s^2 + i\omega\Gamma)} \cdot \frac{(\omega^2 + \omega_s^2 - i\omega\Gamma)}{(\omega^2 + \omega_s^2 - i\omega\Gamma)} = \frac{\omega_s^2(\omega^2 + \omega_s^2 - i\omega\Gamma)}{(\omega^2 + \omega_s^2)^2 + (\omega\Gamma)^2}$$
$$f'_s = \frac{\omega_s^2(\omega^2 + \omega_s^2)}{(\omega^2 + \omega_s^2)^2 + (\omega\Gamma)^2}$$

The scattering factor can be rewritten

and since  $\Gamma \ll \omega_s$ 

the second term being the dispersion correction whose real and imaginary components can be extracted

$$f_{s} = \frac{\omega^{2} + -\omega_{s}^{2} + i\omega\Gamma - (-\omega_{s}^{2} + i\omega\Gamma)}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$= 1 + \frac{\omega_{s}^{2} - i\omega\Gamma}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\approx 1 + \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$
$$\chi(\omega) = f_{s}' + if_{s}'' = \frac{\omega_{s}^{2}}{(\omega^{2} + \omega_{s}^{2} + i\omega\Gamma)}$$

$$\chi(\omega) = \frac{\omega_s^2}{(\omega^2 + \omega_s^2 + i\omega\Gamma)} \cdot \frac{(\omega^2 + \omega_s^2 - i\omega\Gamma)}{(\omega^2 + \omega_s^2 - i\omega\Gamma)} = \frac{\omega_s^2(\omega^2 + \omega_s^2 - i\omega\Gamma)}{(\omega^2 + \omega_s^2)^2 + (\omega\Gamma)^2}$$
$$f'_s = \frac{\omega_s^2(\omega^2 + \omega_s^2)}{(\omega^2 + \omega_s^2)^2 + (\omega\Gamma)^2} \qquad f''_s = \frac{\omega_s^2\omega\Gamma}{(\omega^2 + \omega_s^2)^2 + (\omega\Gamma)^2}$$

# Single oscillator dispersion terms

These dispersion terms give resonant corrections to the scattering factor

## Single oscillator dispersion terms

These dispersion terms give resonant corrections to the scattering factor

$$f_{s}' = \frac{\omega_{s}^{2}(\omega^{2} + \omega_{s}^{2})}{(\omega^{2} + \omega_{s}^{2})^{2} + (\omega\Gamma)^{2}}$$



## Single oscillator dispersion terms

These dispersion terms give resonant corrections to the scattering factor

$$f_{s}^{\prime} = \frac{\omega_{s}^{2}(\omega^{2} + \omega_{s}^{2})}{(\omega^{2} + \omega_{s}^{2})^{2} + (\omega\Gamma)^{2}}$$

$$f_{s}^{\prime\prime} = \frac{\omega_{s}^{2}\omega\Gamma}{(\omega^{2} + \omega_{s}^{2})^{2} + (\omega\Gamma)^{2}}$$

