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The longitudinal electronic response of a sodium monolayer

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Abstract. A point lattice model, with parameters adjusted to fit *ab initio* band-structure calculations for a sodium monolayer, is used to determine the longitudinal response to an external potential as a function of frequency and wavevector. The imaginary part of the response shows loss peaks associated with both inter-band and collective excitations. An energy-loss peak observed for a sodium monolayer on an aluminium substrate is explained qualitatively by the results of this calculation.

1. Introduction

Many techniques used to study surfaces, such as electron energy-loss spectroscopy, differential surface reflectance and electroreflectance with p-polarised light, attenuated total reflection, and surface photoemission, involve the response of the surface to an external scalar potential. For a metal the screening of the external scalar potential by charges induced near the surface is an important effect which must be included in the calculation of this response.

The free-electron model has been studied extensively. If the metal is described using a local (Drude) dielectric function, the induced charge is in an infinitesimally thin layer on the surface. There is a large body of literature on more accurate treatments of surface effects, in which the induced charge is smeared out in a physically realistic manner (Newns 1972, Inglesfield and Wikborg 1975, Griffin and Harris 1976, Feibelman 1982, Maniv and Metiu 1982, Persson and Apell 1983, Gerhardts and Kempa 1984). The most accurate of these theories is the time-dependent local-density approximation (TDLDA), where the electronic wavefunctions and potential are found self-consistently for a uniform jellium background with a sharp edge, and the exchange–correlation potential is added to the Coulomb potential both in the calculation of the ground-state properties and in calculating the screening of the time-dependent external potential (Liebsch 1985, Gies *et al* 1987).

Relatively little work has been done on the inclusion of lattice structure in calculations of surface response. Mochan and Barrera (1985) developed a general theory for the electromagnetic response of an inhomogeneous system, and a similar formalism, starting with a tight-binding band-structure calculation, was used to determine crystalline-induced anisotropy in the optical reflectivity of pure Si and H-covered Si for normally

incident light (Del Sole and Fiorino 1984, Selloni *et al* 1986). Other tight-binding model calculations for insulators have been reported (Wu and Hanke 1977, Inkson and Sharma 1985), and recently the electron energy-loss spectrum for a semimetal (graphite) has been calculated (Palmer *et al* 1987). A calculation of the band structure of a thin Ag film showed that a crystalline-induced surface state could explain electroreflectance measurements with normally incident light (Ho *et al* 1980, Kolb *et al* 1980).

A two-step jellium model of alkali metal overlayers on Al has been treated by Lang (1971) using the local-density approximation. This free-electron model is satisfactory for understanding 'global' ground-state properties such as the electronic charge distribution and work function. However, detailed calculations of the dynamic response of such systems (Eguiluz and Campbell 1985) indicate that a free-electron model is not adequate for explaining observed electron energy-loss spectra (Jostell 1979, Hohlfeld 1986). The purpose of this paper is to present a simple method for including lattice structure in calculations of the response of metallic systems. As an initial application of the method, we will treat a free-standing sodium monolayer.

2. Band structure of a monolayer

In a very simple treatment of a sodium monolayer by Ishida and Tsukada (1986), each sodium atom is represented by two points at which the amplitude of the conduction electron wavefunction is defined. This model gives an s state and a single p state per atom, and contains an energy parameter which can be adjusted to fit the s-p energy difference for an isolated sodium atom. We shall use a model that can describe the true lattice structure more accurately and gives a better fit to *ab initio* band-structure calculations. We introduce a discrete lattice of points \mathbf{r}_μ at which the wave function $\psi(\mathbf{r}_\mu)$ is defined. The eigenvalue equation is

$$\sum_{\nu} H_{\mu\nu} \psi(\mathbf{r}_\nu) = E \psi(\mathbf{r}_\mu). \quad (1)$$

If the Hamiltonian matrix elements are written as $H_{\mu\nu} = T_{\mu\nu} + V_{\mu} \delta_{\mu\nu}$, it is evident that equation (1) is the finite-difference form of the Schrödinger equation $(\mathbf{T} + V)\psi(\mathbf{r}) = E\psi(\mathbf{r})$ where the diagonal term $V_{\mu} \delta_{\mu\nu}$ is the potential energy $V(\mathbf{r}_\mu)$ and the matrix with elements $T_{\mu\nu}$ is the finite-difference form of the kinetic energy operator \mathbf{T} . With a sufficiently fine lattice of points, equation (1) would be an accurate form of the single-particle Schrödinger equation. With a coarse lattice, which must be used for a practical calculation, the elements $H_{\mu\nu}$ are regarded as adjustable parameters which can be chosen to give the best fit to accurate band-structure calculations. This method is thus similar in spirit to empirical tight-binding or $\mathbf{k} \cdot \mathbf{p}$ methods.

We adjust the parameters in our model to fit an *ab initio* calculation of the band structure of a hexagonal Na monolayer (Wimmer 1983). Bulk FCC Na (a fictitious crystal, since Na is BCC) can be formed by piling up such layers. An appropriate point lattice for a bulk FCC crystal is also FCC, with half the spacing of the true lattice. The nuclei occupy a quarter of the points on every other hexagonal layer. Three hexagonal lattice planes are used for a Na monolayer, as shown in figure 1(a). We replace the position index μ by three indices (i, σ, s) , where $i = 1, 2, 3$ labels the lattice planes located at $z(i)$, σ labels the unit cells, and $s = 1, 2, 3, 4$, the four lattice points on plane i in a unit cell. Using this notation, we have $\mathbf{r}_\mu = z(i)\hat{\mathbf{k}} + \mathbf{r}_{\sigma s}(i)$, $\mathbf{r}_{\sigma s}(i) = \mathbf{R}_\sigma + \rho_{si}$ where $\mathbf{r}_{\sigma s}$, \mathbf{R}_σ , and ρ_{si} lie in the xy

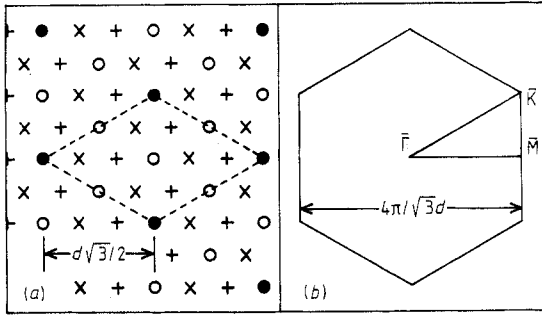


Figure 1. (a) A point lattice representing a Na hexagonal monolayer. The open circles are in the plane $z = 0$, with the full circles at the nuclear positions, the points $+$ are in the plane $z = d/\sqrt{6}$, and the points \times are in the plane $z = -d/\sqrt{6}$, where d is the inter-nuclear distance. The broken line shows a unit cell. (b) The Brillouin zone with symmetry points.

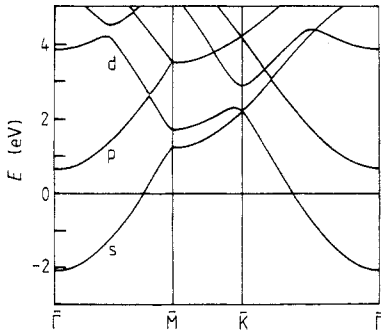


Figure 2. The energy band structure of a Na hexagonal monolayer. The labels s, p, and d denote the main character of a band. The Fermi energy is at $E = 0$.

plane. If we write $\psi(\mathbf{r}_\mu = u(s, i) \exp(i\mathbf{k} \cdot \mathbf{r}_{os}(i))$ where the wavevector \mathbf{k} lies in the xy plane and define

$$H_{is,jt}(\mathbf{k}) = \sum_{\tau} H_{ios,j\tau t} \exp[i\mathbf{k} \cdot (\mathbf{r}_{\tau t}(j) - \mathbf{r}_{os}(i))]$$

equation (1) becomes

$$\sum_{jt} (H_{is,jt}(\mathbf{k}) - E\delta_{ij}\delta_{st})u(t, j) = 0 \tag{2}$$

which can be solved for the energy eigenvalues E_{nk} and eigenvectors $u_{nk}(s, i)$. The calculated band structure, for wavevectors along the triangular path in figure 1(b), is shown in figure 2. We have used only three adjustable parameters: the diagonal energies $H_{\mu\mu} = 0.280$ au at the nuclear positions and 0.180 au at the other points; the off-diagonal energies $H_{\mu\nu} = -0.026$ au for μ, ν nearest-neighbour points, $H_{\mu\nu} = 0$ for more distant points. (The energy units are 1 au = 27.21 eV.) The s and p bands in figure 2 differ from those found by Wimmer (1983) by less than 0.2 eV, but the d band is about 1 eV too high. The fit can be improved by allowing the inter-layer coupling terms $H_{\mu\nu}$ to be different from the intra-layer terms, and by introducing next-nearest neighbour coupling. However, for the problem under discussion the most important bands are the s- and p-like ones, which are properly reproduced at the chosen level of our approximation.

3. Energy-loss spectrum

The longitudinal response function is calculated from the complex susceptibility $\chi(\mathbf{r}, \mathbf{r}', \omega)$ which relates the induced charge $\rho(\mathbf{r}, \omega)$ and an external potential $\varphi_{\text{ext}}(\mathbf{r}', \omega)$ via the symbolic equation $\rho = \chi \varphi_{\text{ext}}$. Taking Fourier transforms in the xy plane, we find

$$\rho(\mathbf{q}, \mathbf{G}, \omega, i) = \sum_{j\mathbf{G}'} \chi(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega, i, j) \varphi_{\text{ext}}(\mathbf{q}, \mathbf{G}', \omega, j).$$

The susceptibility χ is related to χ_0 by the symbolic RPA equation $\chi = \chi_0 + \chi_0 \mathbf{V} \chi$ or

$$\begin{aligned} \chi(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega, i, j) &= \chi_0(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega, i, j) + \sum_{h\mathbf{G}''} \chi_0(\mathbf{q}, \mathbf{G}, \mathbf{G}'', \omega, i, h) \\ &\times V(\mathbf{q}, \mathbf{G}'', h, l) \chi(\mathbf{q}, \mathbf{G}'', \mathbf{G}', \omega, l, j) \end{aligned} \quad (3)$$

where

$$V(\mathbf{q}, \mathbf{G}'', h, l) = (2\pi/A |\mathbf{q} + \mathbf{G}''|) \exp(-|\mathbf{q} + \mathbf{G}''| |z(h) - z(l)|) \quad (4)$$

and

$$\begin{aligned} \chi_0(\mathbf{q}, \mathbf{G}, \mathbf{G}', \omega, i, j) &= \sum_{\substack{nn'k \\ st}} \frac{f_{nk} - f_{n'k+q}}{E_{nk} - E_{n'k+q} + \omega + i\delta} \exp(-i\mathbf{G} \cdot \boldsymbol{\rho}_{si}) \exp(i\mathbf{G}' \cdot \boldsymbol{\rho}_{tj}) \\ &\times u_{nk}^*(s, i) u_{n'k+q}(s, i) u_{n'k+q}^*(t, j) u_{nk}(t, j). \end{aligned} \quad (5)$$

Here, \mathbf{q} is a two-dimensional wavevector, \mathbf{G} , \mathbf{G}' , and \mathbf{G}'' are reciprocal-lattice vectors, i , j , h , and l are lattice plane indices, and A is the unit-cell area. In the calculations we neglect local field effects by setting $\mathbf{G} = \mathbf{G}' = \mathbf{G}'' = 0$. This is the same approximation used previously by Ishida and Tsukada (1986).

It has been shown (Persson and Andersson 1984, Persson and Zaremba 1985) that the surface response function

$$g(\mathbf{q}, \omega) = -\frac{2\pi}{qA} \sum_{ij} \chi(\mathbf{q}, 0, 0, \omega, i, j) \exp[-q(z(i) + z(j) - 2z(1))] \quad (6)$$

is useful for calculating the energy-loss spectrum. Apart from a kinematic factor, the probability for reflecting an electron from the monolayer, with momentum transfer \mathbf{q} parallel to the layer and energy loss ω , is given by $\text{Im } g(\mathbf{q}, \omega)$. In figure 3 the loss function $\omega \text{Im } g(\mathbf{q}, \omega)$ is plotted as a function of ω for selected values of \mathbf{q} along the path $\bar{\Gamma} \rightarrow \bar{M}\dagger$. The full curve shows the result from equation (6), and the broken curve is found using the susceptibility χ_0 , which does not include screening effects, in place of χ in equation (6). In the calculations we have used $d = 6.92$ au for the inter-nuclear distance and $\delta = 0.0055$ au for the width parameter in equation (5).

The dispersion relations for collective and inter-band excitations are shown in figure 4. Collective or plasmon excitations are labelled by c_n , the subscript n denoting the number of zeros in the induced charge density across the monolayer, whereas an excitation corresponding to s-p inter-band transitions is labelled i . The mathematical distinction between the two kinds of excitation modes can be seen by writing the solution of equation (3) in the schematic form $\chi = (\mathbf{I} - \chi_0 \mathbf{V})^{-1} \chi_0$. Collective excitations correspond to zeros in the denominator: $\det(\mathbf{I} - \chi_0 \mathbf{V}) = 0$, and inter-band excitations correspond

† It is convenient to include the factor ω in the loss function so that the areas under the full and broken curves are equal.

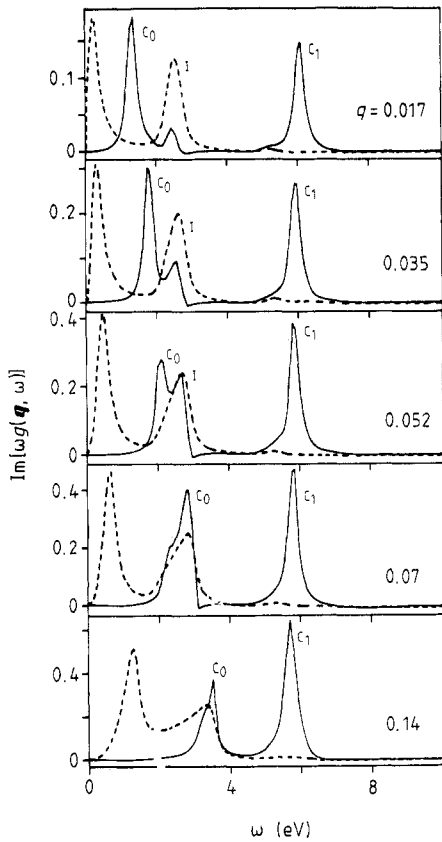


Figure 3. The loss function $\omega \text{Im} g(q, \omega)$, in au, as a function of ω for selected q on the path $\bar{\Gamma} \rightarrow \bar{M}$. The full and broken curves were calculated from χ (with screening) and χ_0 (without screening), respectively. C_0 and C_1 label collective excitations, and I labels an inter-band excitation.

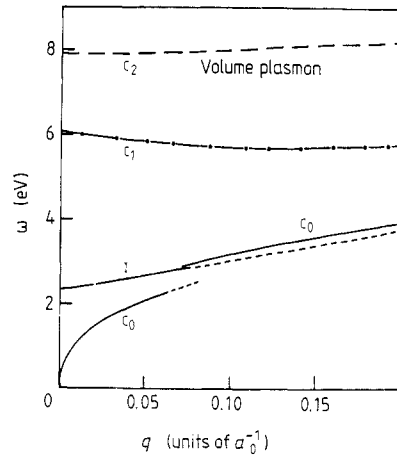


Figure 4. Dispersion relations for the collective and inter-band excitations shown in figure 3.

to peaks in $\text{Im}\chi_0$. In a multilayer film, the excitations C_0 and C_1 become surface plasmons, and a number of excitations C_2, C_3, \dots , appear, which are standing-wave bulk plasmons. These bulk plasmon excitations do not contribute appreciably to the loss function; e.g., the peak from C_2 does not show on the scale of figure (3)†.

4. Discussion

A reflection loss peak at about 2.7 eV has been observed for a sodium monolayer on an aluminium substrate for electrons with an incident energy of 100 eV and a momentum transfer $q = 0.0124a_0^{-1}$ (Hohlfeld 1986). We expect the ‘monopole’ plasmon peak C_0 to be perturbed strongly by the substrate, moving up to an energy of about 10 eV, the surface plasmon energy for Al. The position of the inter-band excitations I should be relatively unaffected by a substrate because they have an effective single-pair character and do not carry a long-range electric field penetrating the substrate. Therefore, if strong

† There is a peak corresponding to the C_2 excitation in the transmission loss function (Ishida and Tsukada 1986).

hybridisation with substrate levels does not occur, these excitations may account for the experimentally observed EELS peaks around 2.5–3.1 eV at low coverages, which are considerably below the surface plasmon frequency of a thick bulk sample of Na. A reflection loss peak at 3.1 eV for a Na monolayer on a Ni substrate has been attributed to an inter-band transition in Na (Jostell 1979). It is possible that the difference between these measured values and the calculated one at 2.4 eV is due to a 'chemical' effect of the substrate and to the fact that the distance between the Na atoms in the overlayer differs from that used in the calculations. For instance, at low coverage, $\theta = \frac{1}{3}$, a well ordered $\sqrt{3} \times \sqrt{3}$ R30° LEED pattern is observed experimentally, which would correspond to an equivalent lattice constant of a freestanding monolayer of Rb. The results of more accurate calculations, which take account of the actual structure of the overlayer and include presence of the substrate, will be reported in the future.

Acknowledgments

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References

- Del Sole R and Fiorino E 1984 *Phys. Rev. B* **29** 4631
- Eguiluz E and Campbell A 1985 *Phys. Rev. B* **31** 7572
- Feibelman P J 1982 *Prog. Surf. Sci.* **12** 287
- Gerhardt R R and Kempa K 1984 *Phys. Rev. B* **30** 5704
- Gies P, Gerhardt R and Maniv T 1987 *Phys. Rev. B* **35** 458
- Griffin A and Harris J 1976 *Can. J. Phys.* **54** 1396
- Ho K-M, Harmon B and Liu S H 1980 *Phys. Rev. Lett.* **44** 1531
- Hohlfeld A 1986 *PhD Thesis* Freie Universität Berlin
- Inglesfield J E and Wikborg E 1975 *J. Phys. F: Met. Phys.* **5** 1706
- Inkson J C and Sharma A C 1985 *J. Phys. C: Solid State Phys.* **18** 5435
- Ishida H and Tsukada M 1986 *Surf. Sci.* **169** 225
- Jostell U 1979 *Surf. Sci.* **82** 333
- Kolb D M, Boeck W, Ho K-M and Liu S H 1980 *Phys. Rev. Lett.* **47** 1921
- Lang N D 1971 *Phys. Rev. B* **4** 4234
- Liebsch A 1985 *Phys. Rev. B* **32** 6255
- Maniv T and Metiu H 1982 *J. Chem. Phys.* **76** 696, 2697
- Mochan W L and Barrera R 1985 *Phys. Rev. B* **32** 4984, 4989
- Newns D M 1972 *Phys. Lett.* **39A** 341
- Palmer R E, Arnett J F and Willis R 1987 *Phys. Rev. Lett.* **58** 2490
- Persson B N J and Andersson P 1984 *Phys. Rev. B* **29** 4382
- Persson B N J and Apell P 1983 *Phys. Rev. B* **27** 6058
- Persson B N J and Zaremba E 1985 *Phys. Rev. B* **31** 1863
- Selloni A, Marsella P and Del Sole R 1986 *Phys. Rev. B* **33** 8885
- Wimmer E 1983 *J. Phys. F: Met Phys.* **13** 2313
- Wu C W and Hanke W 1977 *Solid State Commun.* **23** 829