Additional contributions of electronic structure to elastic anomalies in metallic superlattices

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In our previous paper [Phys. Rev. B **46**, 10 423 (1992)], we studied the contribution of electronic structure to elastic anomalies in metallic superlattices, and focused on the sum of energy eigenvalues term in the Kohn-Sham formulation of the total energy. In this paper, we consider the effects of other terms in the total energy. These terms give contributions to the singularities in the elastic behavior of lower order than those due to the sum of energy eigenvalues obtained previously. This supports our earlier conclusion that, although electronic effects lead to singularities in the variation of elastic constants with modulation wavelength, the features are small and we expect them normally to make no significant contribution to the elastic properties of real materials.

I. INTRODUCTION

Singularities in the total energy resulting from the interaction of the Fermi surface with the Brillouin-zone boundaries introduced by composition modulation are generally recognized as a possible explanation for elastic anomalies observed in metallic superlattices. Recently, we have studied the form of these singularities and their effect on the elastic moduli.[1] We found that although the Fermi-surface–Brillouin-zone interaction does lead to singularities in the total energy and hence in the elastic constants, these singularities are weak and are unlikely to give observable effects in real systems. However, only the sum of energy eigenvalues term in the total energy was considered as this was thought to be the source of the most important singularities. In this paper, we will study the effects of other terms in the total energy.

According to the Kohn-Sham method[2] of density-functional theory,[3] the total electronic energy of the system can be written as

$$E_v[n]=\sum_{i=1}^{N}\epsilon_i-\frac{1}{2}\int\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}'+E_{\rm xc}[n]-\int\frac{\delta E_{\rm xc}[n]}{\delta n(\mathbf{r})}n(\mathbf{r})d\mathbf{r}\ , \tag{1}$$

where $n(\mathbf{r})$ is the electron density, $E_{\rm xc}$ is the exchange-correlation energy functional, and ϵ_i are the Kohn-Sham single-particle energies. We see that the total energy can be separated into three parts: the sum of energy eigenvalues, the corrections due to double counting of the electron-electron interaction in the sum of eigenvalues, and a similar exchange-correlation correction. The latter two corrections depend explicitly on the electron density, thus any singularities there may be in the electron density could induce singularities in these terms, and hence in the total energy.

In our previous study of the sum of eigenvalues contribution, the perturbing potential acting on the electrons due to the composition modulation was characterized by a Fourier component V_g, which we assumed to be a constant. This leads to a singular term in the energy of the form of $(g-g_c)^{5/2}\theta(g-g_c)$ for a system with a quadratic Fermi surface near the Brillouin-zone Fermi-surface contact point at $g=g_c$, where $g=2\pi/\lambda$, λ being the modulation wavelength, and $\theta(x)$ is the step function.[4] However, there may be additional singularities because the perturbing potential will give rise to a small change in the electron density, which in turn, through self-consistency, will modify the effective single-particle potential that generates the sum of eigenvalues, thus introducing a change in the sum of eigenvalues and hence the total energy. Therefore, if singular terms in the density arise, with the same origin as those in the sum of eigenvalues, then there will be additional singularities in the total energy, over and above those we have already treated. These will appear in correction terms to the energy which will be of three types: the electrostatic energy correction, the exchange-correlation energy correction, and the correction to the sum of eigenvalues due to the change in the effective potential. We note that Williams and Weaire[5] in their study of the effect on the energy of Brillouin-zone Fermi-surface contact using the model we have adapted, reported that the correction terms described above introduced new singularities giving an infinite discontinuity in the second derivative of the energy at the contact point. Such a singularity, although it carried little weight, would be one order more severe than the one we found in the sum of eigenvalues and could affect our conclusions on the elastic anomalies. We will calculate the electron density first, then evaluate its effects on the singularities in the total energy.

II. NEARLY-FREE-ELECTRON CASE

A. Electron density

As in our previous study, we consider the nearly-free-electron case first. The electron density is given in terms

of the Kohn-Sham orbitals

$$n(\mathbf{r}) = \frac{2\Omega}{(2\pi)^3} \int_{E(\mathbf{k})<E_F} |\psi_{\mathbf{k}}(\mathbf{r})|^2 \, d\mathbf{k} \, , \tag{2}$$

where the integration is over all occupied states in $\mathbf{k}$ space, and Ω is the crystal volume.

Near the Brillouin-zone boundary at $\mathbf{g}/2$ the wave functions can be approximated by two plane waves as follows:

$$\psi_{\mathbf{k}}(\mathbf{r}) = C_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + C_{\mathbf{k}-\mathbf{g}} e^{i(\mathbf{k}-\mathbf{g})\cdot\mathbf{r}} \, , \tag{3}$$

where $C_{\mathbf{k}}$ and $C_{\mathbf{k}-\mathbf{g}}$ are found from the secular equation to be

$$C_{\mathbf{k}-\mathbf{g}} = F C_{\mathbf{k}} = \frac{1}{\sqrt{\Omega}} \frac{F}{\sqrt{1+F^2}} \, , \tag{4}$$

and $F = [E(\mathbf{k}) - \frac{1}{2}k^2]/V_g$.

As for the calculation of the sum of eigenvalues, we can separate the electron density into a contribution, $n_b(\mathbf{r})$, from the region near the Brillouin-zone boundary, which contains all the singular features of the density, and the remainder which we expect to be analytic near the contact points. We will concentrate on $n_b(\mathbf{r})$. Using wave functions given by Eq. (3), the electron density is

$$n_b(\mathbf{r}) = \frac{2}{(2\pi)^3} \int d\mathbf{k} + \frac{4}{(2\pi)^3} \left(\int \frac{F}{1+F^2} d\mathbf{k} \right) \cos(gz) \, , \tag{5}$$

where the integrations are performed only over the regions near the Brillouin-zone boundary.

We consider the A point at which the lower band first contacts the zone boundaries. In our model, F is

$$\begin{aligned} F &= \frac{1}{V_g} \left\{ E_{g-} + \tfrac{1}{2}k_x^2 + \tfrac{1}{2}k_y^2 - \frac{\alpha_-}{2} \left(\frac{g}{2} - k_z \right)^2 - \tfrac{1}{2}k^2 \right\} \\ &= \frac{1}{V_g} \left\{ E_{g-} - \frac{\alpha_-}{2} \left(\frac{g}{2} - k_z \right)^2 - \tfrac{1}{2}k_z^2 \right\} \, . \end{aligned} \tag{6}$$

The integrand in Eq. (5) may be expanded for $\mathbf{k}$ close to $\mathbf{g}/2$ and the integral performed to yield the following form for the electron density when δE_F is small:

$$\begin{aligned} n(\mathbf{r}) = n_0(\delta E_F) + [\gamma_-(-\delta E_F)^{3/2} + o(-\delta E_F)^{5/2}] \\ \times \cos(gz)\theta(-\delta E_F) \, , \end{aligned} \tag{7}$$

where $\gamma_- = -\frac{\sqrt{2}}{3\pi^2\sqrt{\alpha_-}}$. In Eq. (7), $n_0(\delta E_F)$ is an analytic function of $\delta E_F = E_F - E_{g-}$, where E_F is the Fermi energy and E_{g-} is the top of the lower band.

We note that the superlattice modulation leads to a contribution to the electron density which is nonanalytic in δE_F and which is oscillatory with the superlattice period. This explicit nonanalytic contribution to the electron density will affect the self-consistent Kohn-Sham potential and in particular the Fourier component V_g which also enters the electron density. Such an effect should be incorporated in the calculations of the total energy. Now n is a function of V_g and δE_F, while V_g is a function of n. We want to know the total dependence of n on δE_F so that we can determine the effect of the electron density on the singularities in the total energy.

The calculation is straightforward, and we obtain

$$n(\mathbf{r}) = n_0'(\delta E_F) + \delta n(\mathbf{r}) \, , \tag{8}$$

where

$$\delta n(\mathbf{r}) = [\eta_-(-\delta E_F)^{3/2} + o(-\delta E_F)^{5/2}] \cos(gz)\theta(-\delta E_F)$$

and the coefficient η_- is independent of δE_F and δV_g, which is the additional contribution to V_g due to the electron redistribution. Obviously, the leading singularity in $n(\mathbf{r})$ is still of the order of $(-\delta E_F)^{3/2}$. Calculations proceed in a similar fashion at the B point at which the Fermi surface first breaks through the Brillouin-zone boundary, and we obtain the same results as those in Eq. (8), except that the results for $\delta E_F < 0$ and $\delta E_F > 0$ are interchanged. The leading singularity is at $\delta E_F = 0$, of the order of $(\delta E_F)^{3/2}$. These are significant results because it is straightforward to show that $\delta E_F \propto (g - g_c)$ and consequently the singularity in the electron density has the form $\delta n(\mathbf{r}) \propto (g-g_c)^{3/2}\theta(g-g_c)$, which is a more severe singularity, by one order, than that we found in the sum of eigenvalues contribution to the energy.

B. Influence of electron density on the total energy

In this section we regard δn as a small correction to the analytic part of $n(\mathbf{r})$, and use perturbation theory to estimate the effects of the singular part δn on the various contributions to the total energy in the Kohn-Sham formulation.

For a small change $\delta n(\mathbf{r})$, the change in the Kohn-Sham effective potential is

$$\delta v_{\text{eff}}[n;\mathbf{r}] = \int \frac{\delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} \delta n(\mathbf{r}') d\mathbf{r}' \, . \tag{9}$$

We now use first-order perturbation theory to obtain the effect of δv_{eff} on the Kohn-Sham eigenvalue

$$\delta\epsilon_i = \int \psi_i^*(\mathbf{r}) \delta v_{\text{eff}} \psi_i(\mathbf{r}) d\mathbf{r} = \int |\psi_i(\mathbf{r})|^2 \delta v_{\text{eff}} d\mathbf{r} \, , \tag{10}$$

so the corresponding correction to the sum of eigenvalues is

$$\begin{aligned} \sum_{i=1}^{N} \delta\epsilon_i &= \int n(\mathbf{r}) \delta v_{\text{eff}} d\mathbf{r} \\ &= \int \frac{n(\mathbf{r}) \delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r} \, d\mathbf{r}' \\ &\quad + \int \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')} n(\mathbf{r}) \delta n(\mathbf{r}') d\mathbf{r} \, d\mathbf{r}' \, . \end{aligned} \tag{11}$$

We now consider the change in the electrostatic self-energy and exchange-correlation energy due to the nonanalytic term in the electron density. According to Eq. (1), the change due to δn in these two contributions is

$$\int \frac{\delta E_{\rm xc}[n]}{\delta n}\delta n(\mathbf{r})d\mathbf{r} - \int \frac{\delta E_{\rm xc}[n]}{\delta n}\delta n(\mathbf{r})d\mathbf{r} - \int \frac{\delta^2 E_{\rm xc}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}n(\mathbf{r})\delta n(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' = -\int \frac{\delta^2 E_{\rm xc}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}n(\mathbf{r})\delta n(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' . \quad (12)$$

The total change in the energy to order δn obtained from Eqs. (11), (12), and (1) is, therefore,

$$\delta E_v[n] = \sum_{i=1}^{N}\delta\epsilon_i - \int \frac{n(\mathbf{r})\delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}\,d\mathbf{r}' - \int \frac{\delta^2 E_{\rm xc}[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}n(\mathbf{r})\delta n(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' = 0 . \quad (13)$$

Thus, to first order in δn, the energy is unchanged and the leading correction will be of order $(\delta n)^2$. When we choose, as in Eq. (8), $\delta n \propto \eta_-(-\delta E_F)^{3/2}\theta(-\delta E_F)$ as the perturbation correcting the other parts of the electron density which are analytic in δE_F, we find that the nonanalytic corrections to the density lead to a singularity in the total energy which is of the order of $[(-\delta E_F)^{3/2}]^2\theta(-\delta E_F)$.

C. The minimum properties of the ground-state energy

We can obtain results similar to those in Sec. II B more generally by using the minimum properties of the ground-state energy functional. Suppose we have a ground state with density $n(\mathbf{r})$ and energy $E_v[n]$. Consider a density n_0 close to the ground-state density of the system so that $n = n_0 + \delta n$, where δn is small, and the number of particles is conserved so that $\int \delta n(\mathbf{r})d\mathbf{r} = 0$. We have

$$E_v[n] = E_v[n_0] + \int \frac{\delta E_v[n]}{\delta n}\bigg|_{n_0}\delta n(\mathbf{r})d\mathbf{r} + \frac{1}{2}\int \frac{\delta^2 E_v[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\bigg|_{n_0}\delta n(\mathbf{r})\delta n(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' + \cdots . \quad (14)$$

Noting that

$$\frac{\delta E_v[n]}{\delta n}\bigg|_n = \frac{\delta E_v[n]}{\delta n}\bigg|_{n_0} + \int \frac{\delta^2 E_v[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\bigg|_{n_0}\delta n(\mathbf{r}')d\mathbf{r}' + \cdots \quad (15)$$

we have

$$E_v[n] = E_v[n_0] + \int \frac{\delta E_v[n]}{\delta n}\bigg|_n \delta n(\mathbf{r})d\mathbf{r} - \frac{1}{2}\int \frac{\delta^2 E_v[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\bigg|_{n_0}\delta n(\mathbf{r})\delta n(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' + \cdots . \quad (16)$$

Since $\frac{\delta E_v[n]}{\delta n}|_n = \mu$, the chemical potential which is a constant, and $\int \delta n(\mathbf{r})d\mathbf{r} = 0$, we obtain

$$E_v[n] = E_v[n_0] - \frac{1}{2}\int \frac{\delta^2 E_v[n]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}\bigg|_{n_0}\delta n(\mathbf{r})\delta n(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' + \cdots . \quad (17)$$

Thus the change in $E_v[n]$ is second order in δn.

We now partition the ground-state density n for the superlattice so that n_0 is analytic in δE_F and all the nonanalytic terms are contained in δn. [In the case of nearly-free-electron electrons we would take $\delta n = \eta_-(-\delta E_F)^{3/2}\cos(gz)\theta(-\delta E_F)$.] Then from Eq. (17) the correction to the energy $E_v[n_0]$, which we assume is analytic in δE_F, due to the nonanalytic part of the density δn, is second order in δn, and the leading singularities in the total energy due to δn are of the order $[(-\delta E_F)^{3/2}]^2\theta(-\delta E_F)$. This is the same conclusion as we reached in Sec. II B.

D. Discussion

The effect of the modulation of the superlattice on the singularities in the total energy can be considered as follows: (1) The modulation introduces a perturbing potential, which affects the sum of energy eigenvalues, and leads to a singularity of the order of $(-\delta E_F)^{3/2}$ in the total energy as discussed in our previous paper. (2) This potential leads to a perturbation in the electron density, part of which is nonanalytic in δE_F, of the order of $(-\delta E_F)^{3/2}$ as discussed in Sec. II A. According to the results in Secs. II B and II C, the singularity in the electron density leads to a singularity in the total energy which is of the order of $[(-\delta E_F)^{3/2}]^2\theta(-\delta E_F)$. Thus the singularity in the total energy due to the singularity in the electron density is of lower order than that in the sum of energy eigenvalues due to the perturbing potential alone, which we obtained in our previous paper. This justifies our attention on the sum of energy eigenvalues as the first step in our calculation. Obviously correction terms of the form $[(-\delta E_F)^{3/2}]^2\theta(-\delta E_F)$ in the total energy will give less significant singular behavior in the elastic constants. The dominant singularities in the elastic constants are as we described in our previous paper.

III. OTHER KINDS OF FERMI SURFACE

In the case of the other kinds of Fermi surface discussed in our previous paper, we can also use the two-band model to approximate the wave functions near the zone boundary, and we can calculate the electron density in the same way as we did in Sec. II D. The calculation is straightforward, and we find that the leading singularity in $n(\mathbf{r})$ is the same as that in the number of electrons per atom, and because corrections to the energy are of the order $(\delta n)^2$, these will give lower-order singularities in the total energy and may be disregarded.

IV. CONCLUSION

We can conclude that there are singularities in the electron density which are, in turn, reflected in the per-

turbing potential. These singularities contribute to the singularities in the total energy through the sum of eigenvalues, electrostatic self-energy, and exchange-correlation energy, but their contributions are of lower order than those in the sum of energy eigenvalues as discussed in our previous paper. We can concentrate on the sum of energy eigenvalues when we study the singular behavior in the total energy and in the elastic properties. The correction terms to the total energy do not affect the conclusion in our previous paper on the elastic constants; in particular, we find that electronic effects lead to singularities in the variation of elastic constants with modulation wavelength, but these are weak, and we expect them normally to make no significant contributions to the elastic properties of real metallic superlattices.

Our results, that the sum of the eigenvalues term gives the dominant contribution to the singularity in the total energy, are quite general. But the form of the singularities will depend on the specific form of the band structure near the new Brillouin-zone boundary, and although our results for the sum of eigenvalues, and the density, for different shapes of Fermi surface should be widely applicable, new features may appear in cases in which there is band overlap near the zone boundary and the two-band model may not be adequate.

As we pointed out earlier, Williams and Weaire[5] also treated correction terms to the sum of eigenvalues contribution to the energy and found that the second derivative of the total-energy correction had infinite discontinuities at the contact points, with which we disagree. Their calculation only achieved approximate self-consistency, and imprecise cancellation of the various corrections to first order in δn would lead to a spurious residual correction of order δn rather than $(\delta n)^2$ which would account for their results.

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