Density-functional-theory formulation of classical and quantum Hooke's law

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A fundamental property of solid materials is their stress state. Stress state of a solid or thin film material has profound effects on its thermodynamic stability and physical and chemical properties. The classical mechanical stress (σ^M) originates from lattice strain (ε), following Hooke's law: $\sigma^M = C\varepsilon$, where C is elastic constant matrix. Recently, a new concept of quantum electronic stress (σ^{QE}) is introduced to elucidate the extrinsic electronic effects on the stress state of solids and thin films, which follows a quantum analog of classical Hooke's law: $\sigma^{QE} = \Xi(\Delta n)$, where Ξ is the deformation potential of electronic states and Δn is the variation of electron density. Here, we present mathematical derivation of both the classical and quantum Hooke's law from density functional theory. We further discuss the physical origin of quantum electronic stress, arising purely from electronic excitation and perturbation in the absence of lattice strain ($\varepsilon = 0$), and its relation to the degeneracy pressure of electrons in solid and their interaction with the lattice.

stress in the solid, quantum electronic stress, quantum Hooke's law, density functional theory

1   Introduction

Stress state in the solid and thin film is a fundamental property that greatly affects their thermodynamic stability and physical and chemical properties [1–4]. It have been exploited in a broad range of applications like making and growing new nanostructures [5–8], electromechanical devices [9], mechanochemical sensors [10], and flexible electronics [11]. Classically, lattice stress in a solid is considered a mechanical stress (MS, σ^M) induced by any form of lattice distortion, such as lattice expansion and compression, doping of foreign atoms, or formation of defects (e.g. vacancy). Quantitatively, the mechanical stress follows the classical Hooke's law in linear proportional to lattice strain (ε) as $\sigma^M = C\varepsilon$, where C is elastic constant matrix. Recently,

a new concept of quantum electronic stress (QES, σ^{QE}) is introduced to elucidate the extrinsic electronic effects on the stress state of solids and thin films, in the absence of lattice strain [12]. The QES arises generally from any form of electronic excitation and perturbation when the atomic lattice is fixed, such as photo electronic excitation, charge doping, and quantum confinement effect.

We may simply illustrate the difference between MS and QES using a one-dimensional (1D) lattice, as shown in Figure 1. For a 1D lattice under compressive or tensile lattice strain (ε) (Figure 1(a)), the atomic lattice deformation energy can be expressed as $E = (1/2)C\varepsilon^2 L$, where C is the Young's modulus here but elastic constants in general and L is the length of lattice. By definition, the lattice deformation induced mechanical lattice stress can be expressed as $\sigma^M = (1/L)(dE/d\varepsilon) = C\varepsilon$, i.e. the classical Hooke's law. Now consider an equilibrium lattice without strain ($\varepsilon = 0$), but elec-

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tronically perturbed or excited, for example, an electron is kicked out by a photon leaving behind a hole as shown in Figure 1(b). This electronic excitation process will redistribute the electron density, and the associated "electronic deformation" energy can be expressed as $E=\mu\Delta N$, where μ is the electron chemical potential and ΔN is the change of number of electrons. Then the lattice stress induced by the electronic deformation, which is called QES, can be expressed as $\sigma^{QE}=(1/V)(dE/d\varepsilon)=\Xi\Delta n$, where $\Xi=d\mu/d\varepsilon$ is the deformation potential and Δn is the change of electron density. This equation of $\sigma^{QE}=\Xi\Delta n$ can be viewed as a quantum Hooke's law, expressing the linear dependence of QES on variation of electron density.

The QES is related to electron degeneracy pressure (EDP) of an electron gas. EDP results from the Pauli exclusion principle which disallows two electrons from simultaneously occupying the same quantum state. When increasing the electron density, the emergent repulsive force is manifested as a positive internal pressure, tending to expand the volume of the electron gas; in contrast, when decreasing the electron density, a negative internal pressure appears tending to shrink the volume. Although the QES in the solid is closely related to the EDP of an electron gas, resulting from the same underlying physical mechanism, their dependence on the electron density is quite different, due to the additional electron-ion interaction (i.e. ionic potential) in the solid.

In the following, we will first review the dependence of EDP on electron density for both free electron gas and interacting homogeneous electron gas in Section 2. Then, we will formally derive the classical and quantum Hooke's law for the MS and QES in the solid, respectively, within density functional theory (DFT) in Section 3. In Section 4, we will show calculations of QES induced by charge carrier using first-principles DFT method. Lastly in Section 5, we will discuss the relationship between QES in a solid and EDP of electron gas, and provide a brief summary.

2 EDP of free and interacting homogeneous electron gas

2.1 EDP of free electron gas

For a non-interacting free electron gas, the total energy contains only the kinetic energy term (assuming zero temperature and ignoring thermal pressure), which can be expressed as

$$E_{tot}=\frac{3}{5}V\frac{\hbar^2}{2m_e}\left(3\pi^2\right)^{2/3}\rho^{5/3},\tag{1}$$

where V is the volume of electron gas, m_e is the electron mass, ρ is the electron density. The EDP can be calculated like the normal pressure for ordinary gas as

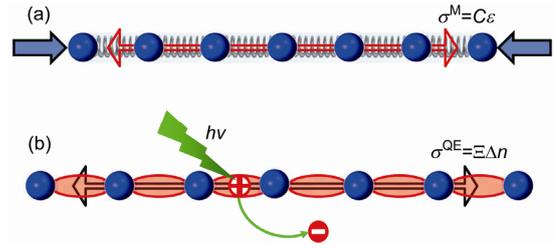$$P=-\frac{dE}{dV}=\frac{\hbar^2}{5m_e}\left(3\pi^2\right)^{2/3}\rho^{5/3}.\tag{2}$$

Figure 1 (Color online) Schematic illustration of MS versus QES. (a) The MS (σ^M) induced by applying a compressive lattice strain (ε). (b) The QES (σ^{QE}) induced by a hole excited by a photon. Arrows indicate stress and force directions. Adopted from ref. [12].

The positive pressure means that free electron gas always tends to expand.

2.2 EDP of interacting homogeneous electron gas

For an interacting electron gas, we need to include the exchange energy and correlation energy of electrons. For simplicity, we use local density approximation (LDA), and the total energy of a homogeneous electron gas is expressed as

$$E=V\times\varepsilon(\rho)\times\rho,\tag{3}$$

where $\varepsilon(\rho)$ is the total energy per electron of a homogeneous electron gas with density ρ; it contains terms of kinetic energy, exchange energy and correlation energy:

$$\varepsilon(\rho)=\varepsilon_T(\rho)+\varepsilon_x(\rho)+\varepsilon_c(\rho).\tag{4}$$

The kinetic energy is the same as that for the free electron gas (eq. (1)). The exchange energy can be expressed analytically as

$$\varepsilon_T=\frac{3}{10}\left(3\pi^2\right)^{2/3}\rho^{2/3},\tag{5a}$$

$$\varepsilon_x=-\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3}.\tag{5b}$$

For convenience, we use atomic units in this section.

Usually for a homogeneous electron gas, another variable r_s is used instead of ρ with

$$\frac{4}{3}\pi r_s^3=\frac{1}{\rho}.\tag{6}$$

Then, the total energy per electron can be expressed as

$$\varepsilon(r_s)=\frac{1.1049}{r_s^2}-\frac{0.4582}{r_s}+\varepsilon_c(r_s).\tag{7}$$

In general, there is no analytical expression for $\varepsilon_c(r_s)$, so it is calculated numerically. We use the Vosko-Wilk-Nusair interpolation formula to calculate $\varepsilon_c(r_s)$, which gives very good results in the density range we are interested [13]:

$$\varepsilon_c\left(r_s\right) = A\left\{\ln\frac{x^2}{X(x)} + \frac{2b}{Q}\arctan\frac{Q}{2x+b}\right.$$
$$\left. - \frac{bx_0}{X(x_0)}\left[\ln\frac{(x-x_0)^2}{X(x)} + \frac{2(b+2x_0)}{Q}\right]\arctan\frac{Q}{2x+b}\right\},$$

(8)

where $x=\sqrt{r_s}$, $X(x)=x^2+bx+c$, and $Q=\sqrt{4c-b^2}$. The parameters A=0.0621814, x_0=−0.10498, b=3.72744, c=12.9352 give the best fitting to Ceperley and Alder's quantum Monte Carlo results [14].

The EDP of an interacting homogeneous electron gas is also calculated numerically using $P=-dE/dV$. Figure 2 shows the EDP induced by different energy terms in eq. (4) as well as the total EDP. One sees that the kinetic energy always induces positive pressure (P_T), tending to expand the volume; while both the exchange and correlation energy induce negative pressure (P_x and P_c), tending to shrink the volume. At very low electron density, the exchange and correlation terms dominate (increasing faster with the increasing density); at high density, the kinetic term dominates. This gives rise to a minimum total EDP, as shown by the inset in Figure 2. Without the inclusion of exchange and correlation energy, the EDP of a free electron gas is always positive and increases monotonically with the electron density; with the inclusion of exchange and correlation energy, it has a minimum at a relatively low electron density, and the overall magnitude of total pressure is greatly reduced, staying below 1 GPa for a large range of electron density.

3 Derivation of classical and quantum Hooke's law within DFT

Within DFT [15], the total energy functional of a solid is expressed as

$$E\left[\rho(\vec{r}),\{\vec{R}_m\}\right] = E_{\text{kin}}\left[\rho(\vec{r})\right] + E_{e-e}\left[\rho(\vec{r})\right]$$
$$+ E_{\text{ext}}\left[\rho(\vec{r}),\{\vec{R}_m\}\right] + E_I\left[\{\vec{R}_m\}\right]$$
$$= E_e\left[\rho(\vec{r})\right] + E_{\text{ext}}\left[\rho(\vec{r}),\{\vec{R}_m\}\right] + E_I\left[\{\vec{R}_m\}\right],$$

(9)

where $E_e\left[\rho(\vec{r})\right]$ is the electronic energy functional of charge density $\rho(\vec{r})$, including kinetic energy $E_{\text{kin}}\left[\rho(\vec{r})\right]$ and electron-electron interaction energy $E_{e-e}\left[\rho(\vec{r})\right]$. $E_{\text{ext}}\left[\rho(\vec{r}),\{\vec{R}_m\}\right]$ is the ion-electron interaction energy, $E_I\left[\{\vec{R}_m\}\right]$ is the ion-ion interaction energy, and $\{\vec{R}_m\}$ are atomic coordinates. We assume $\rho_0(\vec{r})$ and $\{\vec{R}_m^0\}$ are the equilibrium ground-state electron density and atomic coordinates, respectively.
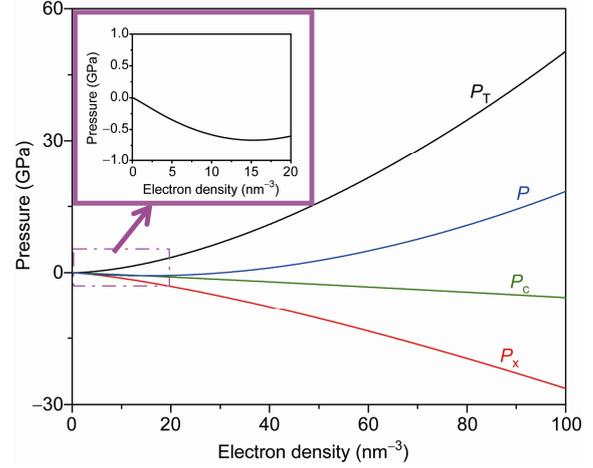

Figure 2 (Color online) Degeneracy pressure induced by different energy terms and the total pressure vs. electron density. Inset shows the total degeneracy pressure for an interacting homogeneous electron gas in the low density range.

3.1 Derivation of classical Hooke's law

Consider the lattice is under a homogeneous strain $\{\varepsilon_{ij}\}$, and the ground-state electron density and the atomic coordinates becomes $\rho_\varepsilon(\vec{r})$ and $\{\vec{R}_m^\varepsilon\}$. By definition, the stress tensor is expressed as

$$\sigma_{ij}^{\text{M}} = \frac{1}{V}\frac{dE\left[\rho(\vec{r}),\{\vec{R}_m\}\right]}{d\varepsilon_{ij}}\bigg|_{\rho_\varepsilon,\{\vec{R}_m^\varepsilon\}} = \frac{1}{V}\left[\frac{\delta E_e\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})}\frac{\partial\rho(\vec{r})}{\partial\varepsilon_{ij}}\right.$$
$$\left. + \frac{\delta E_{\text{ext}}}{\delta\rho(\vec{r})}\frac{\partial\rho(\vec{r})}{\partial\varepsilon_{ij}} + \sum_m\frac{\partial E_{\text{ext}}}{\partial\vec{R}_m}\frac{\partial\vec{R}_m}{\partial\varepsilon_{ij}} + \frac{\partial E_{\text{Ion}}}{\partial\varepsilon_{ij}}\right]_{\rho_\varepsilon,\{\vec{R}_m^\varepsilon\}}$$
$$= \frac{1}{V}\left[\left(\left(\frac{\delta\left(E_e+E_{\text{ext}}\right)}{\delta\rho(\vec{r})}\right)\frac{\partial\rho(\vec{r})}{\partial\varepsilon_{ij}}\right) + \frac{\partial E_R}{\partial\varepsilon_{ij}}\right]_{\rho_\varepsilon,\{\vec{R}_m^\varepsilon\}},$$

(10)

where $E_R=E_{\text{ext}}+E_I$. Since $\rho_\varepsilon(\vec{r})$ is the ground-state electron density under strain, according to Hohenberg-Kohn theorem [15], we have

$$\left(\frac{\delta\left(E_e+E_{\text{ext}}\right)}{\delta\rho(\vec{r})}\right)_{\rho_\varepsilon} = 0,$$

(11)

and eq. (10) becomes

$$\sigma_{ij}^{\text{M}} = \frac{1}{V}\left[\frac{dE_R\left[\rho_\varepsilon(\vec{r}),\{\vec{R}_m\}\right]}{d\varepsilon_{ij}}\right]_{\{\vec{R}_m^\varepsilon\}}.$$

(12)

When applying strain, the transformation of atomic coordinates can be expressed as

$$\{\vec{R}_m^\varepsilon\} = (I+\boldsymbol{\varepsilon})\{\vec{R}_m^0\},$$

(13)

where ε stands for the strain tensor $\{\varepsilon_{ij}\}$, I is the rank-two identity matrix. Then E_R can be expanded with respect to ε as

$$
\begin{aligned}
E_R\left[\left\{\vec{R}_m^\varepsilon\right\}\right] &= E_R\left[\left\{\vec{R}_m^0\right\}\right] + \sum_m \boldsymbol{\varepsilon}\cdot\vec{R}_m^0\cdot\left(\frac{\partial E_R}{\partial\vec{R}_m}\right)_{\vec{R}_m^0}^{\mathrm{T}} \\
&\quad + \frac{1}{2!}\sum_m\left[\left(\boldsymbol{\varepsilon}\cdot\vec{R}_m^0\cdot\left(\frac{\partial}{\partial\vec{R}_m}\right)^{\mathrm{T}}\right)^2 E_R\right]_{\vec{R}_m^0} + \dots \\
&= E_R\left[\left\{\vec{R}_m^0\right\}\right] + \sum_m\sum_{ij=1}^3 \varepsilon_{ij}R_{mj}^0\left(\frac{\partial E_R}{\partial R_{mi}}\right)_{\vec{R}_m^0} \\
&\quad + \frac{1}{2!}\sum_m\sum_{ijkl=1}^3 \varepsilon_{ij}\varepsilon_{kl}R_{mj}^0 R_{ml}^0\left(\frac{\partial^2 E_R}{\partial R_{mi}\partial R_{mk}}\right)_{\vec{R}_m^0} + \dots, \quad (14)
\end{aligned}
$$

where $i, j, k, l = 1$ to 3 are the Cartesian axes.

The MS induced by the strain is then

$$
\begin{aligned}
\sigma_{ij}^{\mathrm{M}} &= \frac{1}{V}\left(\frac{\mathrm{d}E_R}{\mathrm{d}\varepsilon_{ij}}\right)_{\vec{R}_m^\varepsilon} = \sum_m R_{mj}^0\left(\frac{\partial E_R}{\partial R_{mi}}\right)_{\vec{R}_m^0} \\
&\quad + \begin{cases} \dfrac{1}{2!}\sum_m\sum_{kl=1}^3 \varepsilon_{kl}R_{mj}^0 R_{ml}^0\left(\dfrac{\partial^2 E_R}{\partial R_{mi}\partial R_{mk}}\right)_{\vec{R}_m^0} + \dots, & ij\neq kl, \\[2ex] \sum_m\sum_{kl=1}^3 \varepsilon_{kl}R_{mj}^0 R_{ml}^0\left(\dfrac{\partial^2 E_R}{\partial R_{mi}\partial R_{mk}}\right)_{\vec{R}_m^0} + \dots, & ij = kl. \end{cases} \quad (15)
\end{aligned}
$$

Because $\left(\dfrac{\partial E_R}{\partial R_{mi}}\right)_{\vec{R}_m^0}$ is the total force acting on atom m

along i direction. At equilibrium, the total force acting on each atom is zero, so the first term in the right of eq. (15) is zero.

Thus, we have the MS expressed as (to the first order of ε_{ij})

$$
\begin{aligned}
\sigma_{ij}^{\mathrm{M}} &= -\sum_{kl=1}^3 c_{ijkl}\varepsilon_{kl} \\
&= \begin{cases} \dfrac{1}{2!}\sum_m\sum_{kl=1}^3 R_{mj}^0 R_{ml}^0\left(\dfrac{\partial^2 E_R}{\partial R_{mi}\partial R_{mk}}\right)_{\vec{R}_m^0}\varepsilon_{kl}, & ij\neq kl, \\[2ex] \sum_m\sum_{kl=1}^3 R_{mj}^0 R_{ml}^0\left(\dfrac{\partial^2 E_R}{\partial R_{mi}\partial R_{mk}}\right)_{\vec{R}_m^0}\varepsilon_{kl}, & ij = kl, \end{cases} \quad (16)
\end{aligned}
$$

where

$$
c_{ijkl} = \begin{cases} -\dfrac{1}{2!}\sum_m R_{mj}^0 R_{ml}^0\left(\dfrac{\partial^2 E_R}{\partial R_{mi}\partial R_{mk}}\right)_{\vec{R}_m^0}, & ij\neq kl, \\[2ex] -\sum_m R_{mj}^0 R_{ml}^0\left(\dfrac{\partial^2 E_R}{\partial R_{mi}\partial R_{mk}}\right)_{\vec{R}_m^0}, & ij = kl, \end{cases} \quad (17)
$$

is the four-rank stiffness tensor with 81 variables, which can be reduced to 21 independent variables by the inherent lattice symmetry. Eq. (16) is the classical Hooke's law as derived from DFT.

We see from the above derivation that the MS also has the electronic contribution, as the ground-state density changes from $\rho_0(\vec{r})$ to $\rho_\varepsilon(\vec{r})$ when strain is applied, so it also requires quantum mechanical derivation as has been done before [16,17]. Such electronic contribution has been termed as quantum (mechanical) stress or electronic stress before. However, the net outcome of MS still follows the classical Hooke's law, depending explicitly only on the atomic coordinates. This is because the effect of ground-state electronic structure can be casted into the atomic and lattice size effect due to the Hohenberg-Kohn theorem. It is why the MS can be modeled by the empirical interatomic potentials, which are explicit functions of only the atomic coordinates even though the potential depends implicitly on the ground-state electronic structure of lattice. Therefore, the electronic contribution to MS is different from the QES we derive below.

3.2 Derivation of quantum Hooke's law

Consider the electron density of a solid is perturbed from the ground state as $\rho^*(\vec{r}) = \rho_0(\vec{r}) + \delta\rho(\vec{r})$. The differentials of the energy functional are

$$
\begin{aligned}
E_e\left[\rho^*(\vec{r})\right] &= E_e\left[\rho_0(\vec{r})\right] + \delta E_e \\
&= E_e\left[\rho_0(\vec{r})\right] + \int_V \frac{\delta E_e\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})}\delta\rho(\vec{r})\mathrm{d}\vec{r}, \quad (18\mathrm{a})
\end{aligned}
$$

$$
\begin{aligned}
E_{\mathrm{ext}}\left[\rho^*(\vec{r})\right] &= E_{\mathrm{ext}}\left[\rho_0(\vec{r})\right] + \delta E_{\mathrm{ext}} \\
&= E_{\mathrm{ext}}\left[\rho_0(\vec{r})\right] + \int_V \frac{\delta E_{\mathrm{ext}}\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})}\delta\rho(\vec{r})\mathrm{d}\vec{r}. \quad (18\mathrm{b})
\end{aligned}
$$

The stress is then

$$
\begin{aligned}
\sigma_{ij}^{\mathrm{QE}} &= \frac{1}{V}\frac{\mathrm{d}E\left[\rho(\vec{r}),\{\vec{R}_m\}\right]}{\mathrm{d}\varepsilon_{ij}}\Bigg|_{\substack{\rho=\rho^*\\\{\varepsilon_{ij}\}=0}} = \frac{1}{V}\left\{\frac{\mathrm{d}\left(E_e\left[\rho(\vec{r})\right]+\int_V\frac{\delta E_e\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})}\delta\rho(\vec{r})\mathrm{d}\vec{r}\right)}{\mathrm{d}\varepsilon_{ij}}\Bigg|_{\rho=\rho_0} + \frac{\mathrm{d}\left(E_{\mathrm{ext}}\left[\rho(\vec{r})\right]+\int_V\frac{\delta E_{\mathrm{ext}}\left[\rho(\vec{r})\right]}{\delta\rho(\vec{r})}\delta\rho(\vec{r})\mathrm{d}\vec{r}\right)}{\mathrm{d}\varepsilon_{ij}}\Bigg|_{\rho=\rho_0} + \frac{\mathrm{d}E_{\mathrm{Ion}}}{\mathrm{d}\varepsilon_{ij}}\right\}_{\{\varepsilon_{ij}\}=0} \\
&= \frac{1}{V}\left\{\frac{\mathrm{d}\left(E_e+E_{\mathrm{ext}}+E_{\mathrm{Ion}}\right)}{\mathrm{d}\varepsilon_{ij}}\Bigg|_{\substack{\rho=\rho_0\\\{\varepsilon_{ij}\}=0}} + \frac{\mathrm{d}\left(\int_V\frac{\delta E_e}{\delta\rho}\delta\rho(\vec{r})\mathrm{d}\vec{r}+\int_V\frac{\delta E_{\mathrm{ext}}}{\delta\rho}\delta\rho(\vec{r})\mathrm{d}\vec{r}\right)}{\mathrm{d}\varepsilon_{ij}}\Bigg|_{\substack{\rho=\rho_0\\\{\varepsilon_{ij}\}=0}}\right\}. \quad (19)
\end{aligned}
$$

The first term in the right of eq. (19) is the stress of strain-free solid, which is zero. Therefore eq. (19) is simplified as

$$\sigma_{ij}^{QE} = \frac{1}{V} \frac{d\left(\int_V \frac{\delta E_e}{\delta \rho} \delta\rho(\vec{r}) d\vec{r} + \int_V \frac{\delta E_{ext}}{\delta \rho} \delta\rho(\vec{r}) d\vec{r} \right)}{d\varepsilon_{ij}} \Bigg|_{\substack{\rho=\rho_0 \\ \{\varepsilon_{ij}\}=0}}$$

$$= \frac{1}{V} \left\{ \int_V \left[\frac{\partial\left(\frac{\delta(E_e+E_{ext})}{\delta\rho} \right)}{\partial\varepsilon_{ij}} \delta\rho(\vec{r}) + \frac{\delta(E_e+E_{ext})}{\delta\rho} \frac{\partial(\delta\rho(\vec{r}))}{\partial\varepsilon_{ij}} \right] d\vec{r} \right\}_{\substack{\rho=\rho_0 \\ \{\varepsilon_{ij}\}=0}}$$

$$= \frac{1}{V} \left\{ \int_V \left[\frac{\partial\mu(\vec{r})}{\partial\varepsilon_{ij}} \delta\rho(\vec{r}) + \mu(\vec{r}) \frac{\partial(\delta\rho(\vec{r}))}{\partial\varepsilon_{ij}} \right] d\vec{r} \right\}_{\substack{\rho=\rho_0 \\ \{\varepsilon_{ij}\}=0}}, \quad (20)$$

where $\mu(\vec{r}) = \delta(E_e+E_{ext})/\delta\rho(\vec{r})$ is the electron chemical potential. At equilibrium, the electron chemical potential in a solid is uniform; the second term at the right of eq. (20) can be expressed as

$$\frac{1}{V} \int_V \mu(\vec{r}) \frac{\partial(\delta\rho(\vec{r}))}{\partial\varepsilon_{ij}} d\vec{r} = \frac{\mu}{V} \int_V \frac{\partial(\delta\rho(\vec{r}))}{\partial\varepsilon_{ij}} d\vec{r}$$

$$= \frac{\mu}{V} \frac{\partial}{\partial\varepsilon_{ij}} \int_V \delta\rho(\vec{r}) d\vec{r} = \frac{\mu}{V} \frac{\partial}{\partial\varepsilon_{ij}} \Delta N, \quad (21)$$

where N is the total number of electrons. Since N does not change with the strain applied, eq. (20) is equal to zero. Then eq. (19) is further simplified as

$$\sigma_{ij}^{QE} = \frac{1}{V} \left[\int_V \frac{\partial\mu(\vec{r})}{\partial\varepsilon_{ij}} \delta\rho(\vec{r}) d\vec{r} \right]_{\substack{\rho=\rho_0 \\ \{\varepsilon_{ij}\}=0}}$$

$$= \frac{1}{V} \left[\int_V \Xi_{ij}(\vec{r}) \delta\rho(\vec{r}) d\vec{r} \right]_{\substack{\rho=\rho_0 \\ \{\varepsilon_{ij}\}=0}}, \quad (22)$$

where $\Xi_{ij}(\vec{r})$ is electron deformation potential, generally it varies with the spatial position within a solid.

For a homogeneous crystalline solid, when the change of electron density is induced by external excitation like photoexcitation and the change of total electron number $\Delta N = \int_V \delta\rho(\vec{r}) d\vec{r}$ is nonzero and small, we can obtain the distribution of $\delta\rho(\vec{r})$ using the Fukui function defined as [18]

$$f(\vec{r}) \equiv \left(\frac{\partial\rho(\vec{r})}{\partial N} \right)_{v(\vec{r})}, \quad (23)$$

which is the differential change in the electron density due

to an infinitesimal change in the number of electrons. The subscript $v(r)$ means that the atomic potential does not change in the absence of strain.

For semiconductor or insulator, the Fukui function of eq. (23) is ill-defined because the electron added stays at the conduction band minimum (CBM), while the electron removed sits at the valence band maximum (VBM). These two bands have different properties, so there will be derivative discontinuity problem. To resolve this problem, two one-side derivative Fukui functions are defined:

$$f^+(\vec{r}) \equiv \left(\frac{\partial\rho(\vec{r})}{\partial N} \right)_{v(\vec{r})}^+ = \lim_{\delta\to 0^+} \frac{\rho_{N+\delta}(\vec{r}) - \rho_N(\vec{r})}{\delta}, \quad (24a)$$

$$f^-(\vec{r}) \equiv \left(\frac{\partial\rho(\vec{r})}{\partial N} \right)_{v(\vec{r})}^- = \lim_{\delta\to 0^+} \frac{\rho_N(\vec{r}) - \rho_{N-\delta}(\vec{r})}{\delta}. \quad (24b)$$

When electrons are added into the solid, the Fukui function of eq. (24a) is used; when electrons are removed, eq. (24b) should be used.

Using the Fukui functions, eq. (22) can be transformed as

$$\sigma_{ij}^{QE} = \frac{\Delta N}{V} \left[\int_V \Xi_{ij}(\vec{r}) f^\pm(\vec{r}) d\vec{r} \right]_{\substack{\rho=\rho_0 \\ \{\varepsilon_{ij}\}=0}} = \Xi_{ij}^\pm \Delta\rho, \quad (25)$$

where

$$\Xi_{ij}^\pm = \int_V \Xi_{ij}(\vec{r}) f^\pm(\vec{r}) d\vec{r}, \quad (26)$$

which are weighted average of $\Xi_{ij}(\vec{r})$ with respect to the Fukui functions, $\Delta\rho$ is the average change of the electron density. When $\Delta\rho$ is positive, use Ξ_{ij}^+, and when $\Delta\rho$ is negative, use Ξ_{ij}^-. $\Xi_{ij}^\pm$ are the electron deformation potentials for the CBM(+) and VBM(−), respectively.

Eq. (25) can be viewed as quantum Hooke's law, in analogy to classical Hooke's law, with σ^{QE}, Ξ and Δn playing the role of σ^M, C and ε, respectively. However, when an electron density redistribution is induced that the total electron number does not change, for example, quantum confinement in nanostructures or electric field effect in piezoelectric materials, the integral form of eq. (22) must be used to calculate the QES.

4 First-principles calculation of QES induced by charge carrier

From the derivation, we can see that the QES is induced by the electron density variation $\rho^*=\rho^0+\delta\rho$, in the absence of strain. It can be effectively viewed as the stress difference between the MS at the perturbed or excited electron density ρ^* and the ground-state density ρ^0. Practically we can calcu-

late the charge carrier induced QES by applying the original Nielsen-Martin formulism at ρ^*. This gives a finite value of QES even without external strain (note that the MS at the ground-state density ρ^0 vanishes at zero strain.)

Now we demonstrate quantum Hooke's law by directly calculating the QES induced by charging doping in a homogeneous system, i.e. by adding or removing electrons from a solid, using first-principles DFT calculations. We choose four systems: Al (metal), Si (elemental semiconductor), GaAs (compound semiconductor) and ZrO_2 (insulator). Figure 3 shows the calculated QES as a function of added or removed electron density. They all show almost perfect linear dependence on density, in agreement with the theory of quantum Hooke's law. Also we see that adding electrons induces compressive QES (negative by convention), while removing electrons (adding holes) induces tensile QES. In plotting Figure 3, the QES value are taken from the diagonal term of the stress tensor along principle axes, since the stress is isotropic for these cubic lattices. In general, electrons or holes may induce anisotropic stress in other lattices, for example, a hexagonal lattice of graphite [12].

From eq. (25), the slope of σ^{QE} vs. $\Delta\rho$ is the electron deformation potential Ξ. For metal, due to the electron-hole (*e-h*) symmetry, $\Xi=\partial E_F/\partial\varepsilon$ is the same for electron and hole. Thus, the slope for electrons and holes is same in Figure 3(a), and $\Xi_{Al}=-10.49$ eV. For semiconductor and insulator, adding electrons reflects the deformation potentials Ξ^{CBM} of the CBM, while adding holes reflects the deformation potentials Ξ^{VBM} of the VBM, and they are different because of *e-h* asymmetry, as shown in Figure 3 for Si, GaAs and ZrO_2. We

obtained $\Xi_{Si}^{CBM}=-8.65$, $\Xi_{Si}^{VBM}=-9.51$; $\Xi_{GaAs}^{CBM}=-9.77$, $\Xi_{GaAs}^{VBM}=-7.33$; $\Xi_{ZrO_2}^{CBM}=-12.36$, $\Xi_{ZrO_2}^{VBM}=-8.87$, which are in good agreement with previous results [19]. The difference between Ξ^{CBM} and Ξ^{VBM} increases with the increasing band gap, in accordance with the increasing *e-h* asymmetry for large gaps.

5   Discussion and summary

The QES in a solid is closely related to the EDP of electron gas. The EDP of electron gas arises from the Pauli exclusion principle where two electrons cannot simultaneously occupy the same quantum state. When increasing the electron density, the added electrons has to occupy higher energy levels, thus the electron gas will try to expand to bring down the energy levels and reduce the total energy. In a solid, although the electrons are confined by the atomic lattice, the added electrons also have to occupy the higher energy states which will induce an internal positive pressure trying to expand the lattice.

One difference between the QES in a solid and the EDP of an electron gas is that EDP is the total pressure generated by the electron gas, it is negative at small electron density and positive at larger density (see the inset of Figure 2). While the QES is the stress difference between the quantum MS at the perturbed electron density (ρ^*) and the ground-state density (ρ^0); it is always negative when adding electrons and positive when removing electrons. Another difference is that in a solid the electrons are also interacting
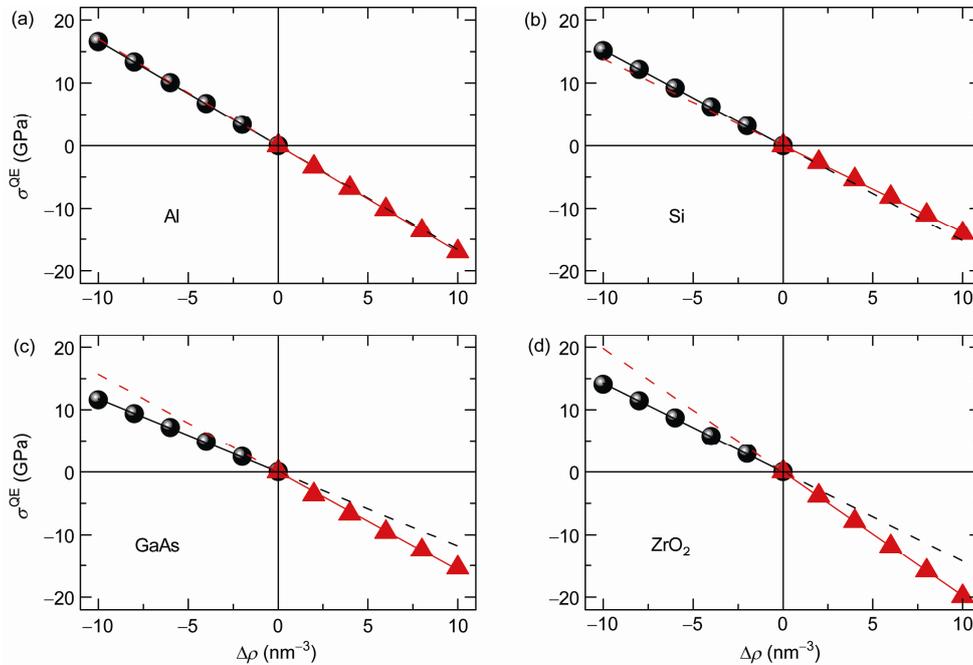

Figure 3   (Color online) The QES induced by electrons (triangles) and holes (circles) as a function of carrier density in (a) Al, (b) Si, (c) GaAs, and (d) ZrO_2. Solid lines are linear fits to the data, and the dashed lines are extensions of the solid lines to indicate different slopes for electrons from holes. The figure is from ref. [12].
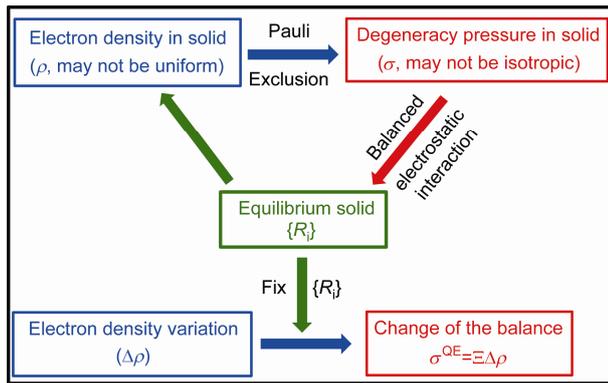
Figure 4 (Color online) Schematic illustration of the origin of QES in a solid in relation to the degeneracy pressure of the electrons as well as the interaction with ions.

with ions, so that the QES is a net outcome of the electrons and ions as well as their interaction, and it follows quantum Hooke's law to vary linearly with the change of electron density; while the EDP of electron gas only involves the electronic degree of freedom but has a complex dependence on electron density (see Figure 2). The third difference lies in the fact the QES in a solid is generally a tensor and anisotropic depending on lattice symmetries, while EDP of electron gas is a scalar and isotropic similar to the pressure of normal gas. In Figure 4, we schematically illustrate the origin of QES in a solid in relation to EDP of an electron gas and electrostatic interactions between electrons and ions.

In summary, we have reviewed a recently introduced concept of QES and derivations of classical and quantum Hooke's within DFT [12]. The physical origin of QES in a solid is discussed is relation to the EDP of an electron gas. The QES and quantum Hooke's law is believed to be applicable to a broad range of physical phenomena and technical applications that couple electronic structure with lattice stress [12], such as semiconductor doping and gating effects, quantum confinement in nanostructures, particle irradiation induced phase transitions, electroelastic and magnetoelastic effects, and biological cell deformation due to charging and polarization.

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