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Quantum Electronic Stress: Density Functional Theory Formulation and Physical Manifestation

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The concept of “quantum electronic stress (QES)” is introduced and formulated within density functional theory (DFT), to elucidate extrinsic electronic effects on the stress state of solids and thin films in the absence of lattice strain. A formal expression of QES (σ^{QE}) is derived in relation to deformation potential of electronic states (Ξ) and variation of electron density (Δn), $\sigma^{QE} = \Xi \Delta n$, as a quantum analog of classical Hooke’s law. Two distinct QES manifestations are demonstrated quantitatively by DFT calculations: (1) in the form of bulk stress induced by charge carriers; and (2) in the form of surface stress induced by quantum confinement. Implications of QES in some physical phenomena are discussed to underlie its importance.

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A fundamental property of solids is their stress state. At the equilibrium lattice constant, the bulk of a crystalline solid is stress free, but the surface has intrinsic non-zero stress and stress is commonly induced by any form of lattice distortion [1]. The stress (strain) state of a solid or thin film has profound effects on its thermodynamic stability and physical and chemical properties [1–3], and has been employed in a wide range of applications such as electromechanical devices [4], mechanochemical sensors [5] and flexible electronics [6], and even to make new nanostructures [7, 8]. Here, we introduce the concept of “quantum electronic stress (QES)” which adds an interesting electronic aspect to our conventional view of “mechanical stress (MS)”. We formulate the expression of QES within DFT, and use DFT calculations to demonstrate quantitatively two distinct physical manifestations of QES, in the form of bulk stress induced by charge carriers in a homogeneous system of crystalline solids and in the form of surface stress induced by quantum confinement in a heterogeneous system of nanoscale thin films. We will then apply the concept of QES to elucidate a few examples of physical phenomena that underlie the importance and usefulness of QES.

Concept of QES. Figure 1 illustrates the fundamental difference between the QES and MS using a simple model of a one-dimensional (1D) lattice. Consider a lattice is under compressive (Fig. 1a) or tensile lattice strain (ε), such as in an epitaxial film due to lattice mismatch between the film and substrate [9, 10]. The “atomic” deformation energy can be expressed as $E = (1/2)Y\varepsilon^2V$, where Y is Young’s modulus and V is the volume of lattice. By definition, the lattice stress induced by the lattice formation, which we refer to here as MS, is expressed as $\sigma^M = (1/V)(dE/d\varepsilon) = Y\varepsilon$, the Hooke’s law. Now, consider an equilibrium lattice in the absence of strain ($\varepsilon = 0$), but electronically perturbed or excited, such as an electron is kicked out by a photon leaving behind a hole, as shown in Fig. 1b, which redistributes

the electron density. The change of electronic energy can be expressed as $E = \mu\Delta N$, where μ is electron chemical potential and ΔN is the change of number of electrons. Then, the lattice stress induced by the electronic change, which we refer to as QES, can be expressed as $\sigma^{QE} = (1/V)(dE/d\varepsilon) = \Xi\Delta n$, where $\Xi = d\mu/d\varepsilon$ is deformation potential and Δn is change of electron density. The expression of $\sigma^{QE} = \Xi\Delta n$ can be viewed as a quantum analog of Hooke’s law. Below, we provide a formal derivation of QES within DFT.

DFT formulation. Following DFT [11], the total energy functional of a solid is written as

$$E[n(\vec{r}), \{\vec{R}_m\}] = E_e[n(\vec{r})] + E_{ext}[n(\vec{r}), \{\vec{R}_m\}] + E_I[\{\vec{R}_m\}] \quad (1)$$

$E_e[n(\vec{r})]$ is the electronic energy functional of charge density $n(\vec{r})$, including kinetic and electron-electron interaction energy, $E_{ext}[n(\vec{r}), \{\vec{R}_m\}]$ is the ion-electron interaction energy, $E_I[\{\vec{R}_m\}]$ is the ion-ion interaction energy and $\{\vec{R}_m\}$ are atomic coordinates. First, for completeness, we briefly review the quantum mechanical derivation of MS. Following the seminal work by

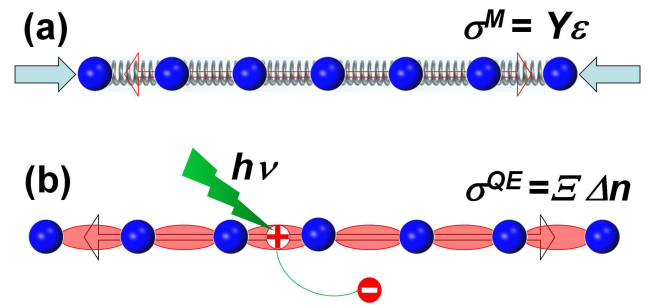


FIG. 1: (Color online) Schematic illustration of MS versus QES. (a) The MS (σ^M) induced by applying a compressive lattice strain (ε). Arrows indicate stress and force directions. (b) The QES (σ^{QE}) induced by a hole excited by a photon.

Nielsen and Martin [12], consider coordinate transformation $\vec{r} = (1 + \{\varepsilon_{ij}\})\vec{r}^0$ and $\vec{R}_m = (1 + \{\varepsilon_{ij}\})\vec{R}_m^0$ under strain $\{\varepsilon_{ij}\}$, where \vec{r}^0 and $\{\vec{R}_m^0\}$ are the electronic and atomic coordinates of strain-free equilibrium lattice. Let $n^0(\vec{r}^0)$ and $n^\varepsilon(\vec{r})$ be the ground-state electron density before and after strain is applied. By definition, the stress tensor is expressed as

$$\begin{aligned} \sigma_{ij}^M &= \frac{1}{V} \frac{dE[n(\vec{r}), \{\vec{R}_m\}]}{d\varepsilon_{ij}} \Big|_{n^\varepsilon, \{\vec{R}_m\}} \\ &= \frac{1}{V} \left[\int_V \left(\frac{\delta(E_e + E_{ext})}{\delta n(\vec{r})} \right) \frac{\delta n(\vec{r})}{\delta \varepsilon_{ij}} d\vec{r} + \sum_m \frac{\partial E_R}{\partial \vec{R}_m} \frac{\vec{R}_m}{\partial \varepsilon_{ij}} \right] \end{aligned} \quad (2)$$

where $E_R = E_{ext} + E_I$. Since $n^\varepsilon(\vec{r})$ is the ground-state electron density at \vec{r} and $\{\vec{R}_m\}$, according to Hohenberg-Kohn theorem [11], we have $\left(\frac{\delta(E_e + E_{ext})}{\delta n(\vec{r})} \right)_{n^\varepsilon, \{\vec{R}_m\}} = 0$ and Eq. (2) becomes

$$\sigma_{ij}^M = \frac{1}{V} \left[\frac{\partial E_R}{\partial \varepsilon_{ij}} \right]_{n^\varepsilon, \{\vec{R}_m\}} \quad (3)$$

For simplicity, assuming hydrostatic strain, $\varepsilon_{ij} = \varepsilon \delta_{ij}$, we expand E_R in ε

$$\begin{aligned} E_R[n^\varepsilon, \{\vec{R}_m\}] &= E_R[n^\varepsilon, \{\vec{R}_m^0\}] + \varepsilon \sum_m \vec{R}_m^0 \left(\frac{\partial E_R}{\partial \vec{R}_m} \right)_{\vec{R}_m^0} \\ &+ \frac{\varepsilon^2}{2} \sum_m \left[\left(\vec{R}_m^0 \cdot \frac{\partial}{\partial \vec{R}_m} \right)^2 E_R \right]_{\vec{R}_m^0} + \dots \end{aligned} \quad (4)$$

Then the MS can be expressed in the first order of ε as the Hooke's law,

$$\sigma^M = \mathbf{K}\varepsilon, \quad (5)$$

where $K = \sum_m \left[\left(\vec{R}_m^0 \cdot \frac{\partial}{\partial \vec{R}_m} \right)^2 E_R \right]_{\vec{R}_m^0}$ is the Bulk modulus.

Next, we derive the QES induced by electronic excitation and perturbation without applying lattice strain ($\varepsilon_{ij} = 0$). Consider a variation of electron density from $n^0(\vec{r}^0)$ the ground-state density at \vec{r}^0 and $\{\vec{R}_m^0\}$ as $n^*(\vec{r}^0) = n^0(\vec{r}^0) + \delta n(\vec{r}^0)$. (Below, for convenience, we will neglect the superscript 0 for \vec{r}^0 .) The differentials of energy functionals are

$$F[n^*(\vec{r})] = F[n^0(\vec{r})] + \int_V \left(\frac{\delta F[n(\vec{r})]}{\delta n(\vec{r})} \right)_{n^0} \delta n(\vec{r}) d\vec{r}, \quad (6)$$

The stress tensor is

$$\begin{aligned} \sigma_{ij}^{QE} &= \frac{1}{V} \frac{dE[n(\vec{r}), \{\vec{R}_m\}]}{d\varepsilon_{ij}} \Big|_{n^*, \varepsilon_{ij}=0} \\ &= \frac{1}{V} \left\{ \int_V \left[\frac{\partial \mu}{\partial \varepsilon_{ij}} \delta n(\vec{r}) + \mu \frac{\partial (\delta n(\vec{r}))}{\partial \varepsilon_{ij}} \right] d\vec{r} \right\}_{n^0, \varepsilon_{ij}=0} \end{aligned} \quad (7)$$

Where $\mu = \partial'_n(E_e + E_{ext})$ is the electron chemical potential. To arrive at Eq. (7), we used the condition that the strain-free ground-state solid is stress free, i.e., $\left(\frac{dE}{d\varepsilon_{ij}} \right)_{n^0, \varepsilon_{ij}=0} = 0$. It can be shown that the second term in Eq. (7) vanishes because chemical potential remains uniform and the number of electrons is independent of strain, so we have the expression of QES as

$$\sigma_{ij}^{QE} = \frac{1}{V} \left[\int_V \frac{\partial \mu}{\partial \varepsilon_{ij}} \delta n(\vec{r}) d\vec{r} \right]_{n^0, \varepsilon_{ij}=0} \quad (8)$$

In a homogeneous crystalline solid, to a good approximation, the electron deformation potential $\Xi = \partial \mu / \partial \varepsilon_{ij}$ is uniform as the electron density remains uniform before and after strain is applied. Then, the expression of QES can be simplified as

$$\sigma^{QE} = \Xi \Delta n \quad (9)$$

Equation (9) can be viewed as a quantum analog of Eq. (5), with σ^{QE} , Ξ and Δn playing the role of σ^M , K and ε , respectively. However, Eq. (8) must be used if Ξ is not uniform in a heterogeneous system. For example, in thin films (hetero-junctions) when strain is applied, charge will be redistributed in the surface (interface) regions due to the nonuniform Ξ .

We emphasize that the MS has its electronic origin; it requires a quantum mechanical derivation as done extensively before [12] because strain changes the ground-state electron density from $n^0(\vec{r}^0)$ to $n(\vec{r})$, whose contribution has been termed as “quantum (mechanical) stress” or “electronic stress”. Yet the net outcome of MS follows classical Hooke's law, depending explicitly only on atomic coordinates. In other words, the effects of the ground-state electronic structure can be cast into the atomic and lattice size effect, having a classical manifestation of MS. It is for this reason that the MS can be modeled by empirical interatomic potential involving explicitly only the atomic degrees of freedom. In contrast, the QES we introduce here has a pure electronic origin involving explicitly the variation of electronic degrees of freedom $[\delta n(\vec{r})]$ that cannot be cast into the atomic or lattice size effect. Consequently, the QES must be described solely by the quantum mechanics of the perturbation of electronic degree of freedom.

Formally, the MS is derived “quantum mechanically” by atomic coordinate transformation $\vec{R}_m = (1 + \{\varepsilon_{ij}\})\vec{R}_m^0$ [12]; while the QES is derived by electron density variation $n^*(\vec{r}^0) = n^0(\vec{r}^0) + \delta n(\vec{r}^0)$ as shown above. Equivalently, we may view the QES as the difference between the quantum MS at the excited/perturbed electron density n^* and that at the ground-state density n^0 . This allows us to practically calculate the QES by applying the original Nielsen-Martin formalism but at n^* instead of n . This gives rise to a finite value of QES even in the absence of external strain (Note that the MS at the ground state

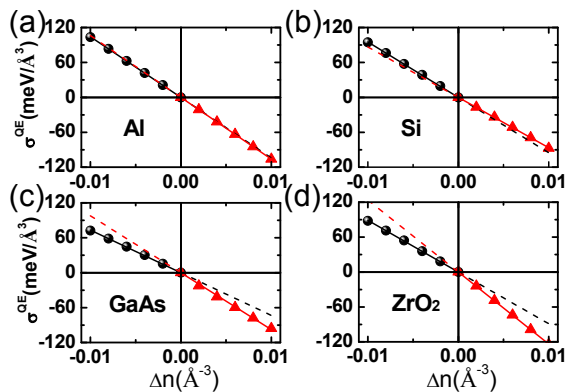


FIG. 2: (Color online) The QES induced by electrons (triangles) and holes (circles) as a function of carrier density in (a) Al, (b) Si, (c) GaAs, and (d) ZrO₂. Solid lines are linear fits to the data, and the dashed lines are extensions of the solid lines to indicate different slopes for electrons from holes.

vanishes at zero strain.). Consequently, the QES underlies a range of stress phenomena induced purely by electronic excitation and perturbation, which are physically different from mechanical deformation induced by strain. Below, using first-principles DFT stress calculations [13], we quantify the magnitude and reveal the nature of QES in two distinct physical manifestations.

QES induced by charge carrier. We first demonstrate the QES for the case of a homogeneous system where Eq. (9) can be applied, in the form of bulk stress when an electron is added to or removed from a solid lattice, such as in the case of semiconductor doping or photo-excited charge carriers in solids. We have calculated the QES induced by adding electrons and/or holes to a finite lattice of Al (metal), Si (elemental semiconductor), GaAs (compound semiconductor) and ZrO₂ (insulator), and graphite (hexagonal lattice). Figure 2 shows the calculated σ^{QE} as a function of Δn for Al, Si, GaAs and ZrO₂, which shows an almost perfect linear dependence for all the cases, in excellent agreement with Eq. (9). In plotting Fig. 2, we have used carrier density ranging from 0 to 6% of the valence electrons, within the typical density variation (up to 10% of the valence electrons) seen in pulse laser experiments but higher than that in doped semiconductors. In general, electrons induce compressive QES (negative by convention); while holes induces tensile QES. In plotting Fig. 2, the QES values are taken from the diagonal terms of stress tensor along principal axes, since stress is isotropic in a cubic lattice. More generally, electrons or holes may induce anisotropic stress, such as in a hexagonal lattice of graphite (see Fig. S1) [13].

According to Eq. (9), the slope of σ^{QE} vs. Δn equals to the deformation potential, Ξ . For a metal, $\Xi = \frac{\partial E_F}{\partial \epsilon}$ is the same for electron and hole because of the electron-hole (e-h) symmetry in the metal, as seen for Al in Fig. 2a, and we found $\Xi_{Al} = -10.49 eV$. For a semiconduc-

tor or insulator, however, the deformation potential for electron ($\Xi^e = \frac{\partial E_{CBM}}{\partial \epsilon}$, CBM stands for conduction band minimum) is different from that for hole ($\Xi^h = \frac{\partial E_{VBM}}{\partial \epsilon}$, VBM stands for valence band maximum) because of the e-h asymmetry, as seen for Si, GaAs and ZrO₂ in Fig. 2. We obtained that $\Xi_{Si}^e = -8.65$, $\Xi_{Si}^h = -9.51$; $\Xi_{GaAs}^e = -9.77$, $\Xi_{GaAs}^h = -7.33$; $\Xi_{ZrO_2}^e = -12.36$, $\Xi_{ZrO_2}^h = -8.87$, which are in good agreement with previous results [14]. In general, the larger the band gap, the larger the e-h asymmetry and hence the larger the difference between Ξ^e and Ξ^h .

We note that conventionally, the deformation potential is derived by calculating the valence and conduction band edge positions as a function of strain, which can be difficult for DFT methods because of the arbitrariness in the absolute value of band energy. Here, our QES calculation provides an efficient and effective method to derive the deformation potential without the need of calculating band structure.

QES induced by quantum confinement. We next demonstrate the QES for the case of a heterogeneous system where Eq. (8) must be applied, in the form of surface stress of nanostructures. We note that the stress effect originated from quantum confinement has been recognized before in the form of bulk strain of nanostructures treated by envelope function approach [15] and in the form of edge stress of graphene nanoribbons calculated from DFT method [16]. Here, we present it as one example illustration for the general concept of QES. Specifically, we will show it in the form of surface QES of nanofilms to distinguish it from the conventional mechanical surface stress.

All the crystalline solid surfaces have a non-zero intrinsic mechanical surface stress with a well-defined magnitude [1, 17], a characteristic surface property of a given film structure. However, if the thickness of a film is

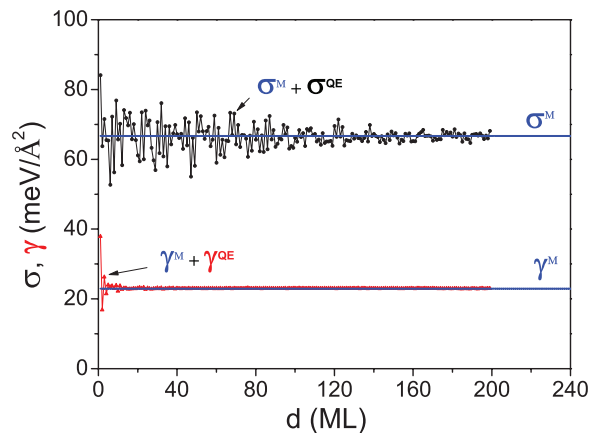


FIG. 3: (Color online) The calculated surface energy and surface stress of Pb(100) film as a function of film thickness, demonstrating the surface QES in metal nanofilms induced by quantum confinement.

reduced to nanoscale comparable to electron Fermi wavelength, quantum confinement becomes prominent giving rise to formation of discrete quantum well states, known as the quantum size effect (QSE) [18, 19]. The QSE has been shown to modify surface energy [20]. Here, we demonstrate that QSE will also modify surface stress, as a distinct manifestation of QES induced by quantum confinement [15, 16].

Figure 3 shows the calculated surface energy (γ) and surface stress (σ) as a function of Pb(100) film thickness (d). γ displays an oscillatory dependence on d , as known before [20]. What's new is that σ displays also an oscillatory dependence on d . The thickness dependence of surface QES can be understood from the thickness dependence of the quantum well states formed in the thin film, which modulates the thin film deformation potential (Ξ) and surface charge density (Δn) as a function of the film thickness. Because both Ξ and Δn are nonuniform in thin film, the simplified expression of Eq. (9) cannot be used (or there would be no QES since $\Delta N = 0$). The results in Fig. 3 are the integrated results of Eq. (8) for each film thickness. Empirically, we may divide the surface energy into mechanical and quantum electronic contributions as $\gamma = \gamma^M + \gamma^{QE}(d)$. Then, by definition, we express surface stress as

$$\sigma = \frac{1}{A} \frac{d\gamma}{d\varepsilon} = \frac{1}{A} \frac{d\gamma^M}{d\varepsilon} + \frac{1}{A} \frac{d\gamma^{QE}}{d\varepsilon} = \sigma^M + \sigma^{QE}(d), \quad (10)$$

where A is surface area, which is also divided into mechanical (σ^M) and quantum electronic contribution (σ^{QE}). γ^M and σ^M represent, respectively, the mechanical surface energy (bond breaking energy) and surface stress (bond deformation energy) of a macroscopic thick film independent of film thickness; γ^{QE} and σ^{QE} represent, respectively, the quantum surface energy and surface stress, arising from quantum confinement in a nanoscale thin film, as a function of film thickness d . As the film thickness increases, γ^{QE} and σ^{QE} will eventually diminish and the system resumes the classical behavior, as shown in Fig. 3.

Implications of QES. We have shown that the DFT calculation of QES provides an effective method for deriving deformation potential without the need of calculating band structure, which circumvents the difficulties encountered by previous methods as well as saves computational time. Physically, the QES induced by charge carriers will help us to better understand the physical nature of semiconductor doping in terms of the dopant-induced lattice stress, by differentiating the QES induced by electrons and holes from the MS induced by size difference between dopant and host atoms [21]. In general, it is easier to dope an element whose QES and MS compensate each other, i.e, small n-type dopants or large p-type dopants, which induce smaller overall amount of stress.

One indirect experimental evidence of QES-related physical phenomenon is the pulse laser induced struc-

tural phase transition, such as the graphite-to-diamond transition [22, 23]. In a pulse lasing experiment, a high density of charge carriers (electrons, holes and excitons) is photo-excited in a small volume for a very short time. We argue that such charge carriers exert a large QES to the local lattice, causing effectively a “pressure-induced” structural phase transition. To support our point of view, we calculated the QES exerted by the photo-excited carriers (holes in the valence bands plus “free” electrons) to an ABC-stack or AB-stack graphite lattice [13]. The QES is found to be tensile and highly anisotropic with the largest component along the z -axis and all the components increase approximately linearly with carrier density (Fig. S1 for the ABS-stack graphite). This is because the QES is dominated by the contribution from holes in the valence band of p_z orbital, as indicated in Fig. 4b. The magnitude of the QES induced by a single hole in the 6-atom cell is as high as 20-30 GPa (Fig. S2), which indicates that the pulse laser can induce a huge “local” stress (pressure) in the graphite lattice, larger than the critical pressure needed for the graphite-to-diamond transitions [24]. Furthermore, we relaxed the graphite structure under the QES exerted by the charge carrier, we directly observed the lattice transformation of graphite into cubic diamond as the QES is gradually decreased upon structural optimization (Fig. s2) [13]. These results shed new lights on the understanding of the pulse laser induced graphite-to-diamond transition, and more generally phase transitions induced by radiation of energetic particles[25].

Furthermore, we propose an experiment to directly observe and measure QES, as illustrated in Fig. 4. One can grow and release a freestanding bilayer strip of cantilever [26], with two lattice-matched semiconductor films but of different band gaps, such as GaAs/AlGa bilayer film. As a photon, whose energy is chosen to be larger than the GaAs gap (1.42 eV) but smaller than the AlAs gap (2.17 eV), comes in it will be only adsorbed by the GaAs layer inducing a QES within it. Consequently, the photoexcitation induced QES in GaAs causes the bilayer to bend and the measurement of bending strain gives a direct measure of the sign and magnitude of QES.

In conclusion, we introduce the concept of QES un-

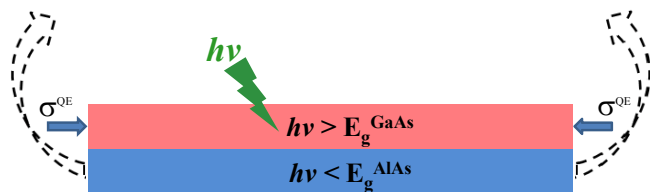


FIG. 4: (Color online) Schematic illustration of an experimental setup to directly measure the QES induced by the photoexcited charge carrier in a semiconductor bilayer cantilever.

derlying the lattice stress induced by electronic excitation/perturbation without external strain as opposed to the conventional strain-induced MS. We derive and confirm by DFT calculation “the law of QES”, as a quantum analog of Hooke’s law of MS. We also propose an experiment to directly measure the charge carrier-induced QES. We expect the QES to manifest broadly in physical phenomena and technological applications that couple electronic structure with lattice stress, 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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