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Chin Shen Ong, Sinisa Coh, Marvin L. Cohen, and Steven G. Louie Phys. Rev. Materials **1**, 075408 — Published 27 December 2017 DOI: 10.1103/PhysRevMaterials.1.075408

Real-space study of the optical absorption in alternative phases of silicon

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(Dated: November 8, 2017)

We introduce a real-space approach to understand the relationship between optical absorption and crystal structure. We apply this approach to alternative phases of silicon, with a focus on the Si₂₀ crystal phase as a case study. We find that about 83% of the changes in the calculated low-energy absorption in Si₂₀ as compared to Si in the diamond structure can be attributed to reducing the differences between the on-site energies of the bonding and anti-bonding orbitals as well as increasing the hopping integrals for specific Si-Si bonds.

I. INTRODUCTION

In order to reduce the cost of solar-cell energy generation, a great deal of effort has been put into attempts to increase the number of charge carriers collected by the solar cell relative to the number of incident photons (quantum efficiency). Silicon is the most widely used photovoltaic material. In terms of global annual power production, a recent market survey shows that crystalline silicon dominates the photovoltaic industry by more than 90%. One of the major reasons for its popularity is that silicon is non-toxic and abundant. There are also benefits from technologies developed over the years in the microelectronics industry.

Despite its widespread usage as a photovoltaic material, silicon does not efficiently absorb most of the light in the solar spectrum. The solar spectrum that is received at the Earth's surface (under the so-called air mass of 1.5 or AM 1.5 for short¹) ranges from 0.3 to 4.4 eV and is the strongest around 1.2 eV. According to the Shockley-Quiesser model,² the optimal band gap from solar energy conversion lies within the range of 1.1 to 1.4 eV.²⁻⁴ Since silicon has a direct band gap of 3.3 eV, optical absorption due to direct transitions can only take place at the highenergy end of the solar spectrum between 3.3 and 4.4 eV. Phonon-assisted indirect transitions^{5,6} lower the onset of optical absorption to 1.2 eV. Even then, absorption coefficients due to indirect transitions alone are smaller and require the solar cell to be thick in order to amplify the phonon contributions. With a thicker absorber layer, the solar cell has to have high purity to prolong its carriers lifetime. Together, the increased thickness and need for material purity add to the cost of production.

Under ambient conditions, the diamond cubic phase (diamond-Si) is the most stable crystal phase of silicon, and this is also the crystal phase of silicon most commonly used to make solar cells today. However, silicon is known to exist in other crystal phases as well. For instance, with increase in pressure, silicon undergoes phase transitions from the diamond-Si phase to the β -Sn phase,⁷ Imma phase⁸, simple hexagonal phase^{9–12} and Cmca phase¹³. Pressure release from the β -Sn phase does

not recover the diamond-Si phase. Instead, a slow pressure release produces the metastable R8 phase¹⁴ which subsequently transforms into the BC8 phase,^{15–18} while a very rapid pressure release leads to two other tetragonal phases.¹⁹ Many of these phases are not suitable to make solar cells. For example, the first four phases mentioned above only exist under high pressure. The β -Sn and simple hexagonal phases are also $metallic^{11,12}$ while the BC8 phase¹⁸ is semi-metallic. On the other hand, phases like the $\mathbb{R}8^{20}$ and body-centered tetragonal²¹ phases are semiconducting, and since they have direct band gaps smaller than diamond-Si's, they in principle can also absorb light over a wider energy $range^{22}$ than diamond-Si. Recently, a low-density silicon allotrope with an open silicon framework consisting of large empty channels, Si_{24} , has reportedly²³ been synthesized. It has a direct G_0W_0 band gap of 1.34 eV, which is smaller than that of diamond-Si.

One approach²² to increasing the absorption range of silicon is then to find a crystal phase of silicon that has a smaller direct band gap than that of diamond-Si. With the advent of first-principles computational techniques, it has become possible to search²⁴⁻²⁷ for crystal phases that have not been previously discovered. Botti *et al.*²⁸ found several crystal phases of silicon that have lower energies than the R8 and BC8 phases and have quasiparticle band gaps ranging from 0.8 to 1.5 eV from GW calculations. Wang $et \ al.^{29}$ proposed phases of silicon that have band gaps from 0.39 to 1.25 eV obtained within density functional theory (DFT) using the hybrid HSE functional. Lee $et al.^{30}$ used the conformational space annealing (CSA) approach and presented several other direct-gap silicon phases. Using the same CSA approach, Oh *et al.*³¹ subsequently proposed a series of direct-gap silicon superlattices composed of bulk-like Si layers intercalated by defective layers made of Seiwatz chains³². Depending on the thicknesses of the bulk-like layers, these superlattices can have calculated G_0W_0 band gaps that fall within the optimal range for solar conversion.

In Ref. 33, Xiang *et al.* found the structure of Si_{20} (also called Si_{20} -T) using the particle swarm optimization (PSO)²⁴ approach. The calculated DFT-HSE band

gap of Si_{20} is 1.55 eV. One of the structural features of Si_{20} , which is not found in diamond-Si, is that some of the bonds form equilateral triangles. In Ref. 33, it was suggested that these bonds might be related to its improved optical absorption. Nevertheless, the microscopic reason for the increase in the calculated absorption in Si_{20} remained unknown. In a related work, Guo *et al.*³⁴ proposed an alternative ground state of silicon with a band gap of 0.61 eV from DFT-HSE that also contains triangular bonds.

The purpose of this work is to understand how the structure of an alternative silicon phase may lead to an improved calculated absorption relative to diamond-Si. While there are many proposed metastable phases of silicon with improved absorption, we focus here in detail on Si₂₀ as a case study for our approach since it has a very desirable calculated optical absorption. (We note that Si₂₀ has a somewhat high formation energy,^{30,35,36} which may make it harder to access experimentally.) To demonstrate the generality of our approach, near the end of this paper, we also study two other silicon phases (SC5 and Si₂₄) that have drastically different structures from that of Si₂₀.

One of the obstacles in establishing the relationship between the crystal structure and optical absorption is the fact that the crystal structures of alternative phases of silicon like Si_{20} and diamond-Si are very different. For example, one cannot be related to the other by the removal or addition of a single atom, or by a small structural distortion that will not drastically disturb the bonding network of the silicon atoms. Moreover, the primitive unit cell of diamond-Si contains two atoms whereas that of Si_{20} contains 20 atoms. Therefore, a conventional analysis of optical absorption in the reciprocal space is non-trivial as each k-point in Si_{20} contains 40 valence and 40 conduction sp^3 -like bands (unlike diamond-Si, which only has four of each).

To overcome this difficulty, we study the optical absorption in a real space representation using Wannier functions. Our analysis reveals that about 33% of the enhanced optical absorption of Si_{20} can be attributed to the decreased differences of the on-site energies between the bonding and anti-bonding orbitals. Roughly 50% is due to the increased hopping integrals between the bonding and anti-bonding orbitals. The remaining 17% is due to a variety of other contributions.

II. METHOD

In this section, we will first describe the conventional density functional theory (DFT) interband-transition approach and the GW plus Bethe-Salpeter equation (GW-BSE) approach for computing optical absorption in reciprocal space. The latter approach includes electron self-energy and electron-hole (excitonic) effects. Next we briefly introduce a real-space representation of the electronic structure in terms of Wannier functions. Finally, we transform the expression for the optical absorption from the reciprocal space representation into the real space representation.

A. Optical absorption

Optical absorption can be expressed through $\epsilon_2(\omega)$, the imaginary part of the dielectric function. Within the independent-particle DFT approach and neglecting the photon momentum, the diagonal elements of $\epsilon_2(\omega)$ can be computed using the random-phase approximation for a specific light polarization,

$$\epsilon_{2}(\omega) = 8\pi^{2}e^{2}\hbar^{2}\sum_{\mathbf{k}}\sum_{n\in\{C\}}\sum_{m\in\{V\}} |\mathbf{e}\cdot\langle n\mathbf{k}|\mathbf{r}|m\mathbf{k}\rangle|^{2} \times \delta(\hbar\omega - E_{n\mathbf{k}} + E_{m\mathbf{k}}).$$
(1)

Here **k** is the wave vector, **e** is the polarization direction, **r** is the position operator, ω is the frequency of absorbed photon, $E_{n\mathbf{k}}$ and $E_{m\mathbf{k}}$ are the DFT eigenvalues, $|n\mathbf{k}\rangle$ and $|m\mathbf{k}\rangle$ are the DFT Bloch eigenstates and $\{V\}$ and $\{C\}$ are the valence and conduction bands. The matrix element $\langle n\mathbf{k}|\mathbf{r}|m\mathbf{k}\rangle$ describes a transition of an electron from state $|m\mathbf{k}\rangle$ into state $|n\mathbf{k}\rangle$ upon the absorption of a photon.

The $\epsilon_2(\omega)$ calculated within the DFT approach is shown in Fig. 1a for diamond-Si (black) and Si₂₀ (red). In this calculation we used a norm-conserving pseudopotential and we used the local density approximation as implemented in Quantum-ESPRESSO.³⁷ The planewave cutoff for the electron wavefunction is 36 Ry. For diamond-Si, the Wannier functions are constructed from a coarse k-mesh of $16 \times 16 \times 16$ and they are used to interpolate quantities on a fine k-mesh of $30 \times 30 \times 30$ to calculate $\epsilon_2(\omega)$. For Si₂₀, the coarse k-mesh is $8 \times 8 \times 8$ and the fine k-mesh is $20 \times 20 \times 20$.

From Fig. 1a, it is clear that within the DFT approach, the onset of optical absorption in Si_{20} is 1.7 eV lower in energy than in diamond-Si. However, absorption of Si_{20} at the absorption edge is relatively small, and it increases significantly only at 0.8 eV above the absorption edge. Comparing the steep edges of the absorption spectra, the steep edge of Si_{20} is still about 0.9 eV lower in energy than it is for diamond-Si.

In what follows, we discuss two well-known limitations of the optical absorption calculated within the DFT-RPA approach. The first limitation is that the calculated DFT-LDA band gap is typically too small due the fact that DFT eigenvalues are not quasiparticle excitation energies. The GW approximation³⁸ removes this limitation by properly including the electron self energy effects. In the case of Si₂₀ and diamond-Si, the inclusion of the GW correction³⁹ separates the DFT valence and conduction bands by 0.7–0.8 eV (depending on the k-points and electron bands) which is close to the value obtained by the hybrid-functional approach in Ref. 33.

The second limitation of the optical absorption calculated within the DFT approach is that it does not



3



FIG. 1. The absorption of diamond-Si (black) and Si_{20} (red) calculated with the DFT (a) and BSE (b) approaches.

consider electron-hole interactions. Within the interacting many-electron picture, an electron is excited from a ground state $|0\rangle$ to an excited excitonic state $|S\rangle$ in which the electron interacts with the hole that it left behind. This process can be calculated⁴⁰ by solving the BSE and $\epsilon_2(\omega)$ is then expressed as,

$$\epsilon_2(\omega) = 8\pi^2 e^2 \hbar^2 \sum_S |\mathbf{e} \cdot \langle S | \mathbf{r} | 0 \rangle |^2 \delta(\hbar \omega - \Omega_S).$$
(2)

Here S labels the exciton states and Ω_S is the exciton eigenenergy.

The $\epsilon_2(\omega)$ spectra calculated³⁹ by solving the BSE for Si₂₀ and diamond-Si are shown in Fig. 1b. Comparing the GW-BSE and DFT absorption spectra, we see two main differences. First, the absorption edge in the GW-BSE spectrum is 0.6 eV higher in energy than the edge in the DFT spectrum. This shift is close to the shift resulting from the GW correction (0.7 eV). The second difference with the GW-BSE approach is that $\epsilon_2(\omega)$ is larger in amplitude by a factor of about 1.5–2.0 near the band edge.

Therefore, while the optical absorption in absolute terms is very different between the GW-BSE and DFT approaches, the corrections made by the GW-BSE approach are nearly the same for both Si_{20} and diamond-Si. To better understand the improved absorption of Si_{20} , it is sufficient to focus on an analysis of results from the DFT-RPA approach, since the geometric effect of the crystal structure is already present at the DFT-RPA level.

B. Localized representation

The Bloch states appearing in the expression for $\epsilon_2(\omega)$ (in Eq. 1) have a well-defined crystal momentum **k**. They are eigenstates of the Kohn-Sham Hamiltonian,

$$\langle n\mathbf{k}|H|m\mathbf{k}\rangle = \delta_{nm}E_{n\mathbf{k}}.$$
 (3)

By superposing the Bloch states of different crystal momenta \mathbf{k} , one can construct a well localized Wannier state,

$$|j\mathbf{R}\rangle = \frac{1}{N_{\mathbf{k}}} \sum_{n\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} U_{nj}^{(\mathbf{k})} |n\mathbf{k}\rangle.$$
(4)

Here **R** is a real-space lattice vector and $U_{nj}^{(\mathbf{k})}$ is an arbitrary unitary matrix that mixes the Bloch bands at **k**. In this paper, we use indices *i* and *j* to denote individual Wannier functions and indices *n* and *m* to denote individual Bloch bands.

One often chooses the matrices $U_{nj}^{(\mathbf{k})}$ according to the scheme introduced by Marzari and Vanderbilt⁴¹ so that $|j\mathbf{R}\rangle$ is as localized in real space around the centers of mass of the Wannier functions as possible. For this reason, $|j\mathbf{R}\rangle$ is also called the maximally localized Wannier function. The Bloch functions can be reconstructed back from the Wannier functions through an inverse transformation,

$$|n\mathbf{k}\rangle = \sum_{j\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} U_{nj}^{(\mathbf{k})\dagger} |j\mathbf{R}\rangle.$$
 (5)

Since the set of Wannier functions contains the same amount of information as the set of Bloch bands from which it is generated, it is convenient to rewrite the Hamiltonian and position operators in the Wannier basis. The Hamiltonian in the Wannier (or real space) representation is simply $\langle i\mathbf{0}|H|j\mathbf{R}\rangle$ which can be calculated by a Fourier transform of $\langle n\mathbf{k}|H|m\mathbf{k}\rangle$,

$$\langle i\mathbf{0}|H|j\mathbf{R}\rangle = \frac{1}{N_{\mathbf{k}}} \sum_{nm\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} U_{ni}^{(\mathbf{k})\dagger} \langle n\mathbf{k}|H|m\mathbf{k}\rangle U_{mj}^{(\mathbf{k})}.$$
 (6)

There are two types of Hamiltonian matrix elements that we will focus on in this paper. For the first type, we have $\mathbf{R} = \mathbf{0}$ and i = j. We will refer to this type of matrix element,

$$\langle i\mathbf{0}|H|i\mathbf{0}\rangle = e_{i,} \tag{7}$$

as the on-site energy of Wannier function i. The remaining matrix elements

$$\langle i\mathbf{0}|H|j\mathbf{R}\rangle = t_{ij\mathbf{R}} \tag{8}$$

(b) Anti-bonding Wannier function

FIG. 2. The isosurface of calculated bonding (a) and antibonding (b) Wannier functions in diamond-Si. Gray spheres are silicon atoms forming the bond. Isosurface in (a) is 1.4 and 1.0 in (b). Red and blue colors indicate parts of the Wannier function with opposite signs.

are known as the hopping integrals. The hopping integral measures the probability amplitude for Wannier function j in cell **R** to tunnel to the Wannier function i in the unit cell at the origin.

Wannier functions are constructed from a set of Bloch bands so a different choice of Bloch bands will lead to different Wannier functions. Since the expression for optical absorption in Eq. 1 refers explicitly to occupied and empty Bloch states, we constructed the Wannier functions either from only empty or only occupied Bloch states. Therefore, by construction, $\langle i\mathbf{0}|H|j\mathbf{R}\rangle$ is zero unless bra and ket are either both derived from empty or occupied states.

We will refer to the Wannier functions constructed from the occupied Bloch states as bonding Wannier functions and those from the empty states of the relevant conduction bands as anti-bonding Wannier functions since they typically have real-space forms that resemble bonding and anti-bonding molecular orbitals. Since silicon bonds are highly covalent, the valence charges are localized on the bonds between these two nearest-neighboring silicon atoms. Therefore, the bonding and anti-bonding Wannier states are localized in the region between these two silicon atoms, as shown in Fig. 2 for the case of diamond-Si. Each Si-Si bond has only one sp^3 -like bonding and one sp^3 -like anti-bonding Wannier function (per each spin). For convenience, we will label the on-site energy for the bonding and anti-bonding states as,

$$e_i$$
 and \bar{e}_i

respectively. Similarly, we denote the hopping integral between anti-bonding states as $\bar{t}_{ij\mathbf{R}}$.

FIG. 3. Conventional unit cell of diamond-Si containing eight silicon atoms. Its primitive unit cell contains only two silicon atoms.

C. Optical absorption in the localized basis

The optical absorption calculated using $\epsilon_2(\omega)$ (Eq. 1) within the DFT-RPA approach depends on the energy of the Bloch states $E_{n\mathbf{k}}$, and the matrix element of the position operator. The Bloch state energies are fully determined by e_i and $t_{ij\mathbf{R}}$. Similarly, the position operator matrix element can be computed from its representation in the Wannier basis

$$\langle i\mathbf{0}|\mathbf{r}|j\mathbf{R}\rangle = \mathbf{r}_{ij\mathbf{R}}.\tag{9}$$

In all, optical absorption is exactly determined given the following three real-space quantities: e_i , $t_{ij\mathbf{R}}$, and $\mathbf{r}_{ij\mathbf{R}}$.

III. RESULTS AND DISCUSSION

In this section, we will compare e_i , $t_{ij\mathbf{R}}$, and $\mathbf{r}_{ij\mathbf{R}}$ in diamond-Si and Si₂₀ and relate them to the structural differences between the two materials, as well as the differences in their optical absorption.

A. Comparison of structures

Figures 3 and 4 show the crystal structures of diamond-Si and Si₂₀. Both of their conventional unit cells have cubic lattices. In our calculations, we use fully relaxed structures of Si₂₀ and diamond-Si. The lattice parameters of the conventional unit cells of Si₂₀ and diamond-Si are 7.40 Å and 5.43 Å. On the average, Si₂₀ has one Si atom every 20.2 Å³ (2.30 g/cm³) and diamond-Si has one atom every 20.0 Å³ (2.33 g/cm³).

Each Si atom in diamond-Si is tetrahedrally coordinated to four other Si atoms, such that every bond angle is exactly 109.5°. Every Si-Si bond in diamond-Si is symmetrically equivalent. The distance between the bond centers of two nearest-neighboring bonds is 1.9 Å.



FIG. 4. Conventional unit cell of Si_{20} containing 20 silicon atoms. Its primitive unit cell is the same as the conventional unit cell. Four distinct Si-Si bonds are indicated with labels a, b, c, and d. Bonds forming a triangle are labelled with letter a.

For Si₂₀, every Si atom is also coordinated to four other Si, but in a distorted tetrahedron. The distortions bring some of the bond centers of Si₂₀ closer together and others further apart. There are four symmetry-inequivalent groups of Si-Si bonds in Si₂₀ and they are labelled from a to d in Fig. 4. One feature of the Si₂₀ structure is the type-a bonds which form triangles. These bonds are highly strained as they are distorted from 109.5° to a narrow 60.0°. As a result, the distance between two nearest-neighboring bond centers ranges from as short as 1.2 Å (between two type-a bonds of the same triangle) to 2.1 Å. We will label this range, 1.2–2.1 Å, as the nearest-neighbor hopping regime.

B. On-site energy e_i

Here we compare on-site energies of diamond-Si and Si₂₀. Since we can assign a single bonding and antibonding Wannier function to each Si-Si bond, we will focus here on comparing the on-site energies, e_i and \bar{e}_i , for the same bond in the crystal.

Calculated values of e_i and \bar{e}_i for diamond-Si and Si₂₀ are shown in Fig. 5 with horizontal lines. The arrow represents the difference between e_i and \bar{e}_i for a given set of symmetry-related bonds in the structure. In the case of diamond-Si, $\bar{e}_i - e_i$ for its Si-Si bond is 9.66 eV. On the other hand, $\bar{e}_i - e_i$ for Si₂₀ ranges from 8.78 to 10.10 eV. The smallest value (8.78 eV) belongs to the highly strained type-a bonds. Its large deviation from diamond-Si's 9.66 eV is likely due to large strain present in these triangular bonds. Less strained type-b and typec bonds have $\bar{e}_i - e_i$ similar to that in diamond-Si (9.64 and 9.78 eV). Finally, type-d bonds have the largest $\bar{e}_i - e_i$ (10.10 eV).

We expect that the smaller $\bar{e}_i - e_i$ of type-a bonds will lower the optical absorption edge of Si₂₀ with respect to diamond-Si's. This will be analyzed in more detail in

FIG. 5. On-site energy of bonding (e_i) , lower value) and antibonding (\bar{e}_i) , higher value) Wannier function in diamond-Si (left, black) and Si₂₀ (right, red). Numbers indicate $\bar{e}_i - e_i$ in eV. In the case of Si₂₀ we show $\bar{e}_i - e_i$ for all four types of bonds. (The origin of the energy scale is arbitrary.)

Sec. III F.

C. Hopping integral t_{ijR}

After analyzing e_i , we now focus on the hopping integral $t_{ij\mathbf{R}}$ of diamond-Si and Si₂₀.

For the analysis of $t_{ij\mathbf{R}}$, we will define the hopping distance as the distance between the centers of mass of the Wannier functions $|i\mathbf{0}\rangle$ and $|j\mathbf{R}\rangle$,

$$\langle i\mathbf{0}|\mathbf{r}|i\mathbf{0}\rangle - \langle j\mathbf{R}|\mathbf{r}|j\mathbf{R}\rangle$$

In what follows, we will relate $t_{ij\mathbf{R}}$ with its hopping distance.

1. Bonding states

First, we discuss the hopping integrals between bonding Wannier functions. As shown in Fig. 6, the hopping integrals of both diamond-Si and Si₂₀ are nearly zero for hopping distances beyond 5 Å. This behavior is characteristic of the exponential localization⁴² of Wannier functions for insulators.

The hopping integral $t_{ij\mathbf{R}}$ with the largest magnitude for diamond-Si is -1.23 eV. This hopping integral couples a bonding Wannier function with its nearest bonding neighbor and has a hopping distance of 1.9 Å. In Fig. 6, it is denoted by the leftmost black dot. For Si₂₀, hopping integrals coupling the nearest bonding neighbors are distributed over the range of 1.2–2.1 Å (see Sec. III A). In Fig. 6, they are represented by the group of red dots surrounding the above-mentioned black dot.

The largest $|t_{ij\mathbf{R}}|$ for Si₂₀ corresponds to the hopping integral with the shortest hopping distance of 1.2 Å. This hopping integral couples type-a bonds and is 0.70 eV





FIG. 6. Hopping integrals between bonding Wannier functions, as a function of hopping distance for diamond-Si (black) and Si_{20} (red).

larger than the largest $|t_{ij\mathbf{R}}|$ of diamond-Si. The presence of this large hopping integral in Si₂₀ is due to the fact that the distance between triangular bonds is 1.9 - 1.2 = 0.7 Å shorter than the shortest bond-bond distance in diamond-Si.

As we will analyze later in more detail, we expect the larger hopping integrals of the occupied Wannier functions to raise the valence band edge in Si_{20} as we expect the valence bands to have a larger bandwidth.

2. Anti-bonding states

Now, we look at the hopping integrals between the anti-bonding states. Figure 7 shows that the largest $|\bar{t}_{ij\mathbf{R}}|$ for diamond-Si is 0.54 eV and has a hopping distance of 5.8 Å. Unlike the bonding states, this largest $\bar{t}_{ij\mathbf{R}}$ does not couple the nearest-neighboring Wannier functions. That hopping integral is four times smaller (0.13 eV). For Si₂₀, the largest $|\bar{t}_{ij\mathbf{R}}|$ is 0.62 eV and has a hopping distance of 3.5 Å. It is somewhat larger than diamond-Si's largest $|\bar{t}_{ij\mathbf{R}}|$ and it also does not couple the nearest-neighboring Wannier functions.

Nevertheless, in the nearest-neighbor hopping regime of 1.2–2.1 Å, the largest $|\bar{t}_{ij\mathbf{R}}|$ in Si₂₀ is 0.40 eV. This value is significantly larger than the corresponding $|\bar{t}_{ij\mathbf{R}}|$ for diamond-Si (0.13 eV) in the same regime.

Notably, even though $|\bar{t}_{ij\mathbf{R}}|$ for anti-bonding Wannier functions are nearly zero above hopping distance of 9 Å, it does not increase monotonically below 9 Å as the hopping distance decreases. The distribution of $\bar{t}_{ij\mathbf{R}}$ (Fig. 7) is more dispersive than that of $t_{ij\mathbf{R}}$ (Fig. 6). This is likely related to the fact that the antibonding Wannier functions (Fig. 2b) have more nodes than the bonding Wannier functions (Fig. 2a). They are also more diffuse than the bonding Wannier functions. In addition, anti-bonding Wannier functions hybridize



FIG. 7. Hopping integrals between anti-bonding Wannier functions, as a function of hopping distance for diamond-Si (black) and Si_{20} (red).

with the continuum, making them somewhat sensitive to the choice of the frozen window used in the Wannier disentanglement⁴³ procedure. (For consistency, we have chosen the frozen windows for both diamond-Si and Si₂₀ to span the same energy range, from the conduction band minimum (CBM) to 3.5 eV above the CBM of diamond-Si.)

Hopping integrals between anti-bonding Wannier states of Si_{20} are distributed over a wider energy range than diamond-Si. We expect the larger hopping integrals between the empty Wannier functions of Si_{20} to increase the bandwidth of the conduction bands and lower its lower band edge. This will be further discussed in Sec. III F.

D. Position integral r_{ijR}

Now we discuss the third real-space object required to compute the optical absorption: position operator in the real space representation, $\mathbf{r}_{ij\mathbf{R}}$, between a bonding Wannier function and an anti-bonding Wannier function. (The matrix elements between two bonding or two antibonding Wannier functions do not enter into Eq. (1).)

For diamond-Si, $|\mathbf{r}_{ij\mathbf{R}}|^2$ is the largest when *i* and *j* are both centered on the same bond, as can be expected. Its value is $|\mathbf{r}_{ij\mathbf{R}}|^2 = 0.59 \text{ Å}^2$ and it is seven times as large than that between the neighboring bonds (0.09 Å²). For Si₂₀, the largest $|\mathbf{r}_{ij\mathbf{R}}|^2$ are also on the same bond. Their values for four types of Si₂₀ bonds are nearly the same. Their average value is $0.53\pm0.02 \text{ Å}^2$. (The next largest value is only 0.15 Å².)

Here, two observations can be made. First, we see that in the real space representation, $|\mathbf{r}_{ij\mathbf{R}}|^2$, like the Hamiltonian, is highly localized. Second, the largest $|\mathbf{r}_{ij\mathbf{R}}|^2$ for Si₂₀ and diamond-Si have nearly the same numerical value. This is likely because the Wannier functions of Si₂₀



FIG. 8. Optical absorption of diamond-Si (black), Si_{20} (solid red), and two hybrid cases (dashed, dotted, see text for details). Absorption curves are scissor shifted by 0.6 eV in all four cases based on our GW-BSE calculation.

have similar real-space character as those in diamond-Si.

E. Relating e_i and t_{ijR} to the optical absorption

Now, we will relate the magnitudes of e_i and $t_{ij\mathbf{R}}$ to the optical absorption in diamond-Si and Si₂₀. For this purpose, we compute the optical absorption in three model systems, which are hybrids between diamond-Si and Si₂₀. These hybrid systems have the same Hamiltonian as Si₂₀, except for some e_i , \bar{e}_i , $t_{ij\mathbf{R}}$ and $\bar{t}_{ij\mathbf{R}}$ which are modified to resemble those in diamond-Si. Figure 8 shows the calculated optical spectra of diamond-Si (in solid black), Si₂₀ (in solid red), and the hybrid systems (in dashed, dotted-and-dashed, and dotted red).

The dashed red curve in Fig. 8 shows the calculated optical absorption of the first hybrid system, where all on-site energies, e_i and \bar{e}_i , of Si₂₀ are made to be equal to those of diamond-Si.

The dotted-and-dashed curve in Fig. 8 represents the second hybrid system where, on top of the modifications made for the first hybrid system, hopping integrals $t_{ij\mathbf{R}}$ between bonding Wannier functions are modified as well. This modification is done in the following way. First, we identify hopping integrals in Si₂₀ larger than the nearest-neighbor hopping integral in diamond-Si (their values are -1.93, -1.45, -1.30, and -1.29 eV). Second, we modify these hopping integrals so that they are equal to the nearest-neighbor hopping integrals so that they are equal to the nearest-neighbor hopping integral in the diamond-Si (-1.23 eV).

Finally, the dotted red curve in Fig. 8 shows the optical absorption of the third hybrid system which, in addition to the modifications made for the first and second hybrid systems, has modified hopping integrals between the anti-bonding Wannier functions, $\bar{t}_{ij\mathbf{R}}$. Here we follow the same logic as is used for hopping integrals between the bonding Wannier functions. We first identify hopping integrals in Si_{20} in the nearest-neighbor regime that are larger than the nearest-neighbor hopping integral in diamond-Si (their magnitudes are 0.18, 0.20, 0.23, 0.32, 0.34, and 0.40 eV). Next, we modify these hopping integrals to the nearest-neighbor hopping integral between anti-bonding states in diamond-Si (0.13 eV).

As can be seen from Fig. 8, modifying only e_i and \bar{e}_i shifts the leading edge of the absorption spectrum of Si₂₀ to a higher energy by about 0.30 eV. This is about 33% of its difference with diamond-Si. Modifying e_i , \bar{e}_i , and $t_{ij\mathbf{R}}$ further shifts the leading edge of the absorption spectrum by another 0.30 eV. When e_i , \bar{e}_i , $t_{ij\mathbf{R}}$ and $\bar{t}_{ij\mathbf{R}}$ are all modified, the edge of the absorption spectrum is shifted by a total of 0.75 eV from the original calculated spectrum which accounts for approximately 83% of its difference with diamond-Si.

This behavior can be understood by considering a simple tight-binding model of a periodic one-dimensional mono-atomic chain. The band structure of such a model is given by $e + 2t \cos(ka)$ where e is the on-site energy, t is the hopping integral between the nearest-neighboring orbitals, and a is the distance between atoms. Therefore, on-site energy e can be thought of as an average energy of the band while the hopping integral t determines its bandwidth. This means that smaller $\bar{e}_i - e_i$ and larger $t_{ij\mathbf{R}}$ and $\bar{t}_{ij\mathbf{R}}$ found in Si₂₀ will lower the average band gap.

The modifications that are made to the hybrid systems do not account for the remaining 17% and an absorption tail at low energy. We attribute this to the following two effects. First, we only modified some of the larger hopping integrals in our calculations of the hybrid models. Second, even though we modified the hopping integrals in our calculations, we have always kept the crystal structure of Si_{20} the same. Therefore, relative phases of the Bloch states between neighboring siliconbond sites will be different in Si_{20} and in diamond-Si. In other words, even if the hopping integrals were somehow made exactly the same in the two structures, their optical absorption edges may still not be the same because of this effect. Nevertheless, the total influence of these two effects on the improved optical absorption of Si_{20} is rather small (17%) and the majority of the difference can be attributed to the changes in the on-site energies and hopping integrals.

F. SC5 and Si₂₄ silicon phases

To demonstrate the generality of our approach, we consider here two other phases of silicon that also absorb light (without phonon-assisted transitions) at photon energy lower than diamond-Si. The first phase can be described as a Si superlattice composed of alternating stacks of bulk-like Si layers intercalated by Seiwatz chains.³¹ Each stack is made of five Si(111) layers of hexagonal diamond-Si. The Seiwatz chains are arranged

in a configuration that results in a simple monoclinic Bravais lattice. We refer to this phase as SC5. The second phase is a low-density Si_{24} structure with an open silicon framework.²³ Unlike Si_{20} we discussed earlier, none of these two phases have Si-Si bonds in a triangular arrangement.

Repeating the earlier analysis for SC5, we find that all of its bonds have $\bar{e}_i - e_i$ smaller than that in diamond-Si. In SC5, they range from 9.09 to 9.61 eV. If we change the on-site energies of SC5 to match those of diamond-Si, we find that the optical spectrum more closely resembles that of diamond-Si. This change in the on-site energies accounts for roughly 70% of the change in the optical absorption. Furthermore, if we also change the hopping integrals of SC5 to match those of diamond-Si, we find another 20% of the change in the optical absorption. Therefore, the improved calculated optical absorption edge of SC5 is mostly due to changes in the on-site energies, not hopping integrals. This is in contrast to Si₂₀ where dominant effect came from the hopping integrals.

Switching now to Si_{24} , our calculation shows that most of the on-site energy differences $(\bar{e}_i - e_i)$ are larger than those in diamond-Si. Out of 24 bonds in the primitive unit cell, 18 have higher on-site energy differences while only six have smaller differences than that of diamond-Si. The range of calculated $\bar{e}_i - e_i$ in Si₂₄ ranges from 9.18 to 10.69 eV. We attribute this to Si_{24} 's open silicon framework and its low density $(2.17 \text{ g/cm}^3)^{23}$ as compared to that of diamond-Si (see Sec. III A). If we modify the onsite energies of Si_{24} so that they are equal to that of diamond-Si, we find that the onset of optical absorption shifts to a lower energy. If we also modify the hopping elements, the optical absorption more closely matches that of diamond-Si. Therefore, we conclude that in the case of Si_{24} , the effect of the on-site energies on the optical absorption is opposite to that of the hopping integrals.

IV. CONCLUSION

The different structure of Si_{20} , relative to diamond-Si, leads to smaller on-site energy differences and larger hopping integrals between some of its Wannier functions. We have identified that most of these differences are due to the strained bonds forming triangles (i.e. type-a bonds) in Si₂₀. Different on-site energies and large hopping integrals are responsible for approximately 83% of the improved optical absorption in Si₂₀ for photovoltaic applications relative to diamond-Si. The remaining difference is attributed to contributions from the smaller hopping integrals and the effect of the crystal structure on the relative phase of the electron wave functions.

Introducing strain to the bonds in the crystal structure turns out to be important when looking for crystal phases of silicon that have band gaps smaller than diamond-Si. However, as strain may reduce the band gap of diamond-Si, it also reduces the stability of the crystal structure. It is possible that a large band gap reduction may require a strain that is too large for the crystal structure to be thermodynamically stable. Hence, in the search for a practically viable silicon crystal phase that has a band gap smaller than that of diamond-Si, it is a balance between reducing the band gap and increasing the strain in the crystal structure.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant No. DMR-1508412 which provided for the DFT calculations and the Wannier functions analysis, and by the Theory of Materials Program at the Lawrence Berkeley National Lab funded by the Director, Office of Science and Office of Basic Energy Sciences, Materials Sciences and Engineering Division, U.S. Department of Energy under Contract No. DE-AC02-05CH11231 which provided for the GW-BSE calculations. Computational resources have been provided by the DOE at Lawrence Berkeley National Laboratory's NERSC facility. C.S.O. acknowledges support from the Singapore National Research Foundation (Clean Energy) PhD Scholarship.

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