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An *ab initio* method is presented to calculate shallow impurity levels in bulk semiconductors. This method combines the GW calculation for the treatment of the central-cell potential with a potential patching method for large systems (with 64,000 atoms) to describe the impurity state wave functions. The calculated acceptor levels in Si, GaAs and an isovalent bound state of GaP are in excellent agreement with experiments with a root-mean-square error of 8.4 meV.

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Semiconductors are useful because their electrical properties can be controlled by intentional doping. While there are deep impurity levels in semiconductors, it is the shallow ones that are most useful for making them n-type or p-type [1] and are also responsible for the rich fine optical spectroscopy that often eludes explanations [2, 3]. Presently, there are ways to calculate deep level energies based on *ab initio* total energy calculations with an accuracy of about 0.2 eV [4-8]. Unfortunately, that is not adequate for shallow impurities because their binding energies are smaller than this threshold. Besides, calculating shallow impurities by such methods would require the total energy calculations of supercells with tens of thousands of atoms [9], which is beyond the current capability. There are hydrogen model treatments of shallow donor and acceptor levels, with either simple effective mass or the k.p method [10, 11]. The resulting binding energies for such methods are independent of the chemistry of the impurity element; but, in reality, the impurity level changes dramatically depending on the impurity element (e.g., from 45.8 meV for Si:B to 247.7 meV for Si:Tl) [12]. This chemical dependence is called the central-cell potential correction, and it has been intensely studied in the 1970s and 1980s [13]. In the simplest picture, this correction can be considered as an additional local potential near the impurity. Phillips has analyzed such central-cell corrections in terms of the atomic elastic potential and chemical potential [14-16]. Other theoretical approaches, including Green's function methods, have been developed to treat the central-cell potential and impurity level calculations [17-20]. However, self-consistent calculations are

difficult to obtain, and sometimes fitting parameters are used to represent the central-cell potential, defying the purpose of predicting the binding energies. Thus, to date, accurate *ab initio* predictions have not been practically attainable. In this paper we present an approach that can accurately predict the binding energies of shallow acceptor levels with a root-mean-square error of 8.4 meV for the systems we tested. This approach combines two techniques, one allowing the calculations of large systems, another providing an accurate central-cell potential using the GW method. Here we focus on acceptor levels since they tend to have larger elemental dependencies.

One of us has previously developed a method for using the local density approximation (LDA) of the density functional theory (DFT) to calculate the central-cell potential and to apply it directly to a shallow impurity level calculation with 64,000 atoms [21]. While it was found that the LDA single-particle Hamiltonian provided the correct trend, it could not yield accurate binding energies [21]. This approach should be able to yield the elastic contribution to the central-cell potential accurately. It thus raises the question of whether the LDA is accurate enough for the chemical contribution. This reminds us of the LDA band alignments problem [22-24]. A more accurate approach is to use the many-body perturbation GW method, which has been demonstrated to provide better band alignments [22-25] and can also be helpful in direct deep impurity level calculations [26]. Here we present an approach that includes the GW effects in shallow impurity calculations.

There are two approaches for calculating the binding energy of an impurity state. One is from the total energy point of view, calculating it as the total energy difference between the E(N) and E(N-1) systems (the energy needed to remove one electron from the impurity to the bulk). This is used for deep level calculations [4, 5, 7]. The second approach is to calculate the eigen-energy of the GW equation (which is equivalent to the total energy difference between the N and N-1 systems [27]). The GW equation can be written as:

$$\left[-\frac{1}{2}\nabla^2 + V(r)\right]\psi_i(r) + \int \Sigma(r,r',\varepsilon_i)\psi_i(r')d^3r' = \varepsilon_i\psi_i(r) \tag{1}$$

Here $V(r) = \sum_R Z/|r-R| + \int \rho(r')/|r-r'|d^3r'$ is the local potential consisting of the ionic potential and Hartree potential calculated from the electron charge density $\rho(r)$, and $\Sigma(r,r',\varepsilon_i)$ is the nonlocal self-energy term. The top of the valence band eigen-energy ε_i of the impurity system, when compared with the bulk value, will give us the impurity binding energy. However, it is presently computationally

impractical to simulate the entire system using the GW method. We therefore seek appropriate approximations in order to solve Eq. (1). There are many versions of self-consistency for GW calculations [25, 28, 29]. We use a version where $\rho(r)$ will be taken from the LDA without further updating. This procedure has been shown to be adequate in band offset studies [22, 24]. As a result, the local potential $V(r)$ in Eq. (1) will be the same as that in the LDA Kohn-Sham (KS) equation, while the LDA exchange and correlation potential $\mu_{xc}(\rho(r))$ is replaced by Σ. The goal is to use a modified potential to approximate the effects of Σ. We further choose the G_0W_0 approximation for GW calculations [25, 28, 29], although our procedure works for any GW approach that does not update $\rho(r)$.

We first consider a large supercell with N electrons. After p-type doping, the neutral system has N-1 electrons. One immediate question is: Should one use N or N-1 electrons for Eq. (1)? For an exact quasiparticle equation, the resulting ε_N is independent of choosing N or N-1 (e.g., the total energy curve E(n) for n between N-1 and N is a straight line) [30]. This holds approximately for the GW equation [31, 32]. However, the KS eigen-energy ε_N calculated from LDA depends sensitively on the total number of electrons (partly due to the erroneous self-interactions [33]). One important fact is that for a closed shell system, where there is a relatively large gap between the highest occupied state and lowest unoccupied state, the GW self-energy $\Sigma(r,r',\varepsilon_i)$ is short ranged in regard to $r-r'$, typically within a distance of 5Å [34, 35]. As a result, we can perform small-system GW calculations and approximate the effects of Σ by some simplified short-range nonlocal potential terms. Thus, we will choose the closed-shell N electron system. In the following paragraphs, we describe how to approximate Eq. (1) in different regions of the impurity system.

The N electron system is −1 charged. As a result, the V(r) will have a $1/\varepsilon r$ long-range potential tail where ε is the dielectric constant of the system. Thus, for a position r far from the impurity, the potential part of the Hamiltonian (for the top of the valence band) can be approximated as:

$$V_{tot} \equiv V(r) + \Sigma(r,r',\varepsilon_{VBM}) \rightarrow V_{bulk}(r) + \Sigma_{bulk}(r,r',\varepsilon_{VBM}) + 1/\varepsilon r \tag{2}$$

The bulk part, $V_{tot}^{bulk} \equiv V_{bulk} + \Sigma_{bulk}$, is short ranged (for $r-r'$) and periodic. Its effects can be represented by the LDA potential V_{bulk}^{LDA} with a correction term. In a plane wave pseudopotential calculation, each atom will have s, p, d nonlocal pseudopotentials (for clarity, we have ignored them in Eqs. (1) and (2)). We have adjusted the s nonlocal pseudopotentials to reproduce the bulk GW effective masses (which have a

large influence on the impurity binding energies), while keeping the LDA bulk valence band maximum (VBM) energies unchanged. In Table S.I of the supplementary material [36] we list the valence band effective masses obtained after the bulk correction for GaAs. For the indirect bandgap systems Si and GaP (Table S.I), the LDA effective masses without correction are already adequate. In Table S.I we have used experimental effective masses as our references, which are close to GW effective masses that we calculated. We call the resulting potential (with the readjusted atomic nonlocal part) V_{bulk}^{LDA+C} .

   Now, for r close to the impurity, the situation is more complicated. As analyzed by Phillips [14, 15], there are two contributions to the central-cell potential. The first is the elastic atomic relaxation and the related potential change near the impurity [14]. This will be treated with LDA calculations. The second is the difference between the electronic structure of the impurity relative and its host [15]. This will be treated with GW calculations. The elastic strain due to a central impurity atom decays as $1/R^3$ [37]. As a result, the atomic displacement becomes very small beyond a supercell size of about 512 atoms (see supplementary material [36]). Thus, a 512-atom supercell is relaxed using the plane wave pseudopotential DFT method (with the VASP code [38-43]). N=2048 valence electrons are used (the Si:X and GaAs:X systems are −1 charged). The resulting potential $V_{512}^{LDA}(r)$ can be used to construct the potential inside the region of the 512-atom box (Ω_{512}), while Eq. (2) is used outside the region. However, V_{512}^{LDA} cannot be connected with Eq. (2) directly for Si:X and GaAs:X, since the as-calculated V_{512}^{LDA} from the −1 charged periodic supercell includes the $1/\varepsilon r$ image potential from the neighboring imaging charges. This image potential can be expressed as:

$$V_{im}(r) = \sum_{(i,j,k)\neq(0,0,0)} \frac{1}{\varepsilon \,|\vec{r} - \hat{x}Li - \hat{y}Lj - \hat{z}Lk\,|} \tag{3}$$

Here, L is the size of the 512-atom supercell. This function can be calculated numerically using FFTs, in a similar way to the evaluation of Ewald energies [44]. Now for $r\in\Omega_{512}$:

$$V_{tot}(r) = V_{512}^{LDA+C}(r) - V_{im}(r) + V_C \tag{4}$$

Here V_C is a constant that is used to shift the potential, so V_{tot} can be matched to the potential outside the Ω_{512} box described in Eq. (2) or, say, $V_{bulk}^{LDA+C}(r)+1/\varepsilon r$. Note that the superscript LDA+C means the same

modified *s* nonlocal potential (e.g., in GaAs) from the bulk fitting is used for host atoms both inside and outside Ω_{512}. The ε is the static dielectric constant which can either be calculated using LDA with a slab technique [45] (which gives the same result as the perturbation theory and allows the calculation of ionic contribution), or directly taken from experimental value to avoid LDA error [36]. Note that based on the symmetry, beyond the spherical $1/\varepsilon r$ term, the potential tail can have a higher order octopole moment term, which decays as $1/r^8$. The fact that the potential inside and outside Ω_{512} can match at the boundary with only a 3 meV error, using only the spherical potentials, indicates that such a high-order effect is rather small beyond Ω_{512} [21].

We have used this approach to construct a large supercell containing up to 64,000 atoms. The Nth eigen-state (top of the valence band) of this system can be calculated using the folded spectrum method (FSM) [46], which solves only a few eigen-states near a given reference energy E_{ref} based on the equation $(H - E_{ref})^2 \psi_N = (\varepsilon_N - E_{ref})^2 \psi_N$. The state ψ_N is the impurity state, and its eigen-energy ε_N minus the bulk VBM energy ε_{VBM} (using bulk V_{bulk}^{LDA+C}) gives us the impurity binding energy. We have found that the impurity state wave function ψ_N can indeed extend to many thousands of atoms [21], and the ε_N change with supercell size is shown in Table I for the case of Si:In. All these findings indicate that the 64,000-atom cell is necessary, similar to the conclusion obtained from tight-binding calculations [9].

As shown in the fourth column of Table II, the binding energies following the above procedure are not accurate enough. We thus turn to the second contribution of the central-cell potential, the electronic structure difference between the impurity atom and the host atoms and its GW treatment. So far, this difference is treated at the LDA level. We expect the difference between $\Sigma(r,r',\varepsilon_{VBM})$ and $\Sigma_{bulk}(r,r',\varepsilon_{VBM})$ to be localized near the impurity; thus, we can use a 64-atom cell to capture this difference. We have carried out GW calculations (using VASP) for 64-atom supercells with one impurity atom (with LDA relaxed atomic positions) using N=256 electrons (the system is –1 charged but with a closed shell).

In order to generate a numerical Hamiltonian that is both compatible with the rest of the V^{LDA+C} potential and also can be used to calculate the 64,000-atom system, we have used the following procedure to transfer the information in the 64-atom GW calculation to the large system calculation. Note that the GW Hamiltonian is obtained by replacing the LDA exchange correlation potential $\mu_{xc}(\rho(r))$ with the GW self-energy term $\Sigma(r,r',\varepsilon_{VBM})$ while keeping the local potential $V(r)$ of Eq. (1) the same as in LDA. This results in a well-defined eigen-energy shift of the 64-atom impurity system

$\Delta\varepsilon_{VBM}^{64} = \varepsilon_{VBM}^{GW}(64) - \varepsilon_{VBM}^{LDA}(64)$ and also an eigen-energy shift of the bulk system $\Delta\varepsilon_{VBM}^{bulk} = \varepsilon_{VBM}^{GW}(bulk) - \varepsilon_{VBM}^{LDA}(bulk)$. Since the bulk VBM energy has been kept fixed in our bulk LDA modification to get V_{bulk}^{LDA+C}, in the current 64-atom LDA adjustment the overall shift for the $\varepsilon_{VBM}^{LDA}(64)$ should be $\Delta\varepsilon_{VBM} = \Delta\varepsilon_{VBM}^{64} - \Delta\varepsilon_{VBM}^{bulk}$ instead of $\Delta\varepsilon_{VBM}^{64}$. This assures that the alignment between the local impurity potential and the bulk potential is the same as in the GW calculations. The calculated $\Delta\varepsilon_{VBM}^{64}$ and $\Delta\varepsilon_{VBM}^{bulk}$ are listed in Table S.II [36] for the systems studied here. We see that the resulting $\Delta\varepsilon_{VBM}$ varies from a few meV to 100 meV. Following in the same procedure as in bulk LDA modification, here we change the *p* nonlocal potentials for the atoms near the impurity to generate the $\Delta\varepsilon_{VBM}$ shift. There are, however, several choices for this fitting representing the range of the impurity nonlocal potential $\Sigma(r,r',\varepsilon_{VBM})$. We have tested three choices: (1) adjusting only the *p* nonlocal potentials on the impurity atom; (2) adjusting the *p* nonlocal potentials of the impurity atom and the four nearest neighbor atoms; and (3) adjusting the *p* nonlocal potentials of only the four nearest neighbor atoms. The fitting is done to generate the desired shift $\Delta\varepsilon_{VBM}$ of the 64-atom supercell while using minimum changes of the *p* potentials (as presented in Table S.III [36]). We found that the final 64,000-atom VBM energy differs less than 1 meV among these three choices, indicating the insensitivity of our final results to the fitting procedure.

Using the 64-atom supercell fitted nonlocal potentials for the impurity atom, the bulk fitted nonlocal potentials for the host atoms (only for GaAs in our cases), the patched LDA local potential of Eqs. (2) and (4), and the FSM [46], we can now calculate the VBM eigen-energies of the 64,000-atom systems. Spin-orbit couplings due to the core levels based on relativistic pseudopotentials are also included in the Hamiltonian. This is important for heavy atom impurities like Tl and Sn. We use LDA+GW to indicate our results. The binding energies for Si acceptors are listed in Table II. We see that the experimental binding energy varies from 45.8 meV to 247.7 meV from B to Tl impurities. Our calculated binding energy changes from 44 meV to 246 meV.

In order to test our procedure for more ionic systems, we have also calculated the acceptor levels of GaAs. One choice is with a column IV element to replace As, such as GaAs:C, GaAs:Si, GaAs:Ge, and GaAs:Sn. Another choice is with a group II element to replace Ga, such as GaAs:Mg. The results are listed in Table III.

Lastly, we have also tested one isovalent impurity level GaP:Bi. When one P is replaced by Bi, a single distinct bound level above the valence band is formed. This is special because the closed-shell N electron system is neutral, and there is no $1/\varepsilon r$ tail on the potential. Thus, in the above procedure, the

potential tail in Eq. (2) should not be added, and V_{im} need not to be subtracted in Eq. (4). In a way, the central-cell potential is solely responsible for the bound state. The calculated binding energy of 41 meV is in excellent agreement with the experimental measurement of 39.7 meV [47].

The calculated binding energies are plotted in Fig. 1 against the experimental values. Our LDA+GW results fall close to the y=x line. Some of the computational details are presented in supplementary materials [36]. To show the difference between the current method and other theoretical approaches, we have also calculated the impurity binding energies using other methods and plotted them in Fig. 1. One approach is to follow the above procedure but without GW correction of the 64-atom calculations. They are denoted as the LDA(eigen) method. They are much smaller than the experimental results, indicating the inadequacy of using the LDA to describe the central-cell chemical potential. We have also used the LDA total energy approach to calculate the impurity binding energy. This is the total energy difference between the E(N) and E(N-1) compared with the bulk VBM eigen-energy, as is often done for deep level calculations [4-8]. We have strictly followed the procedures described in Ref. [5] and have used a 512-atom supercell. The result is shown as LDA(Etot, 512) in Fig. 1. We see that the energy is far away from the experimental result. Furthermore, as the impurity wave function is much larger than the 512-atom supercell [10], this procedure is not converged with respect to supercell size. This can be seen from the results LDA(Etot, infinite), which are based on the same total energy difference formalism [5] but are estimated (instead of directly calculated) from the 64,000-atom system impurity eigen-state calculations (as derived in Ref. [21]). The results are much smaller than the 512-atom results (LDA(Etot, 512)). They are also much smaller than the 64,000-atom LDA results based on the eigen-energy (LDA(eigen)).
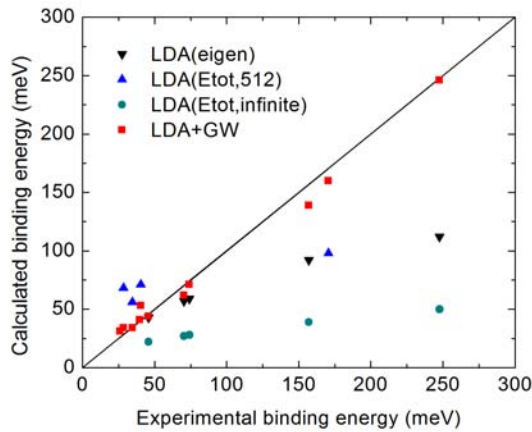
Fig. 1. Calculated binding energies plotted against experimental binding energies. The solid line indicates perfect matching of theoretical results with experimental results. Our final results are LDA+GW.

Finally, our procedure can be summarized as the following well-controlled and tested steps. (1) Correct the bulk LDA nonlocal potential to reproduce the GW or experimental effective masses. (2) Use a 512-atom supercell (with the impurity atom) LDA calculation to relax the atomic positions and generate an LDA local potential V^{512}. (3) Using V^{512}, subtract the image potential to generate the potential inside the 512-atom supercell, and match that to the outside potential (which equals the LDA bulk potential plus a $1/\varepsilon r$ term). This will generate an LDA local potential $V_{LDA}^{64,000}$ for a 64,000-atom supercell. (4) Carry out a 64-atom supercell (with the impurity atom) GW calculation and obtain its VBM eigen-energy shift relative to the LDA result. Fit the impurity atom nonlocal pseudopotentials in the LDA calculation to reproduce this VBM eigen-energy shift in the 64-atom cell. (5) Use the fitted nonlocal potentials from the bulk atom in (1), and the impurity atom in (4), and the $V_{LDA}^{64,000}$ obtained in (3), together with the FSM to solve for the VBM eigen-energy of the 64,000-atom system. The resulting eigen-energy minus the bulk VBM eigen-energy will be the impurity binding energy.

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Table I. Si:In impurity eigen-energy convergence relative to bulk VBM with increasing supercell size L. $\infty*$ indicates the final binding energy extrapolated from that of the smaller sizes. This is for the LDA(eigen) calculation.

Cell size L	4a	8a	16a	20a	$\infty*$
E_{im} (meV)	188	110	92.3	91.7	91.6

Table II. Binding energies of shallow acceptor levels in Si from experimental measurement (E_b(exp)), calculated by hydrogen model (E_b(Hyd)), LDA eigen-energy method (E_b_LDA(eigen)), LDA total energy method with infinite supercell size (E_b_LDA(Etot, infinite)) and "LDA+GW" procedure (E_b(LDA+GW)) as described in the current paper. The unit of the energies is meV.

Host: Imp	E_b (exp) [a]	E_b (Hyd) [b]	E_b_LDA (eigen) [c]	E_b_LDA(Etot, infinite) [c]	E_b(LDA +GW)
Si: B	45.8	31.6	43	22	44
Si: Al	70.4	31.6	57	27	62
Si: Ga	74.2	31.6	59	28	71
Si: In	157.0	31.6	92	39	139
Si: Tl	247.7	31.6	112	50	246

[a]Reference [12].
[b]References [10, 11].
[c]Reference [21].

Table III. Binding energies of shallow acceptors in GaP and GaAs from experimental measurement (E_b(exp)), calculated by "LDA+GW" procedure (E_b(LDA+GW)) and LDA total energy method with 512-atom supercell (E_b_LDA(Etot, 512)).

Host: Imp	E_b (exp)	E_b_LDA (Etot, 512)	E_b (LDA+GW)
GaP: Bi	39.7[a]	--	41
GaAs: C	26.0[b]	--	31
GaAs: Si	34.5[b]	56	34
GaAs: Ge	40.4[b]	71	53
GaAs: Sn	170.5[b]	98	160
GaAs: Mg	28.4[b]	68	34

[a]Reference [47].
[b]Reference [48].

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