

***Ab initio* local vibrational modes of light impurities in silicon**J. M. Pruneda,^{1,*} S. K. Estreicher,² J. Junquera,³ J. Ferrer,¹ and P. Ordejón⁴¹*Departamento de Física, Facultad de Ciencias, Universidad de Oviedo, C. Calvo Sotelo s/n, 33007 Oviedo, Spain*²*Department of Physics, Texas Tech University, Lubbock, Texas 7940 9-1051*³*Departamento de Física de la Materia Condensada C-III, Universidad Autónoma, E-28049 Madrid, Spain*⁴*Institut de Ciència de Materials de Barcelona – CSIC, Campus de la UAB, E-08193 Bellaterra, Spain*

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We have developed a formulation of density-functional perturbation theory for the calculation of vibrational frequencies in molecules and solids, which uses numerical atomic orbitals as a basis set for the electronic states. The (harmonic) dynamical matrix is extracted directly from the first-order change in the density matrix with respect to infinitesimal atomic displacements from the equilibrium configuration. We have applied this method to study the vibrational properties of a number of hydrogen-related complexes and light impurities in silicon. The diagonalization of the dynamical matrix provides the vibrational modes and frequencies, including the local vibrational modes (LVM's) associated with the defects. In addition to tests on simple molecules, results for interstitial hydrogen, hydrogen dimers, vacancy-hydrogen and self-interstitial-hydrogen complexes, the boron-hydrogen pair, substitutional C, and several O-related defects in *c*-Si, are presented. The average error relative to experiment for the ~ 60 predicted LVM's is about 2% with most highly harmonic modes being extremely close and the more anharmonic ones within 5–6% of the measured values.

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I. INTRODUCTION

The knowledge of the structures of impurities and defects is an essential prerequisite for understanding the electrical and optical changes that these complexes induce in semiconductors such as crystalline silicon.^{1,2} The presence of light impurities such as H, B, C, or O results in the appearance of infrared (IR) or Raman-active local vibrational modes (LVM's), usually well isolated from the frequency range of the phonons of the host material. The observation of LVM's, coupled with isotope substitutions and uniaxial stress measurements, provide precious information about the type and number of impurity atoms involved and the symmetry of the defect. However, these data are rarely sufficient to identify the defect unambiguously.

Since the early days of Stein,³ a large number of vibrational modes have been identified through the interplay of experiment and theory. The calculation of LVM's at the *ab initio* level provides a critical link between theory and experiment. This is particularly true in the case of hydrogen, since it binds covalently in the immediate vicinity of many impurities and defects, thus giving rise to a number of LVM's in the range ~ 800 to ~ 2200 cm^{-1} . Other common impurities in Si which produce LVM's are B, C, and O, but any element lighter than Si can in principle be observed by LVM spectroscopy.

The computation of systematically accurate vibrational frequencies is a challenge for first-principles theory, given their sensitivity on the details of bonding geometry and electronic structure. Various approaches have been used to calculate LVM's, from semiempirical models,⁴ to *ab initio* Hartree-Fock⁵ and density-functional theory.^{6–8} Typical accuracies in the calculated vibrational modes for light impurities in silicon in former works are within 3% and 10% of the experimental data, which means in some cases a deviation of over 100 cm^{-1} .

In most cases, frequencies are calculated in the spirit of the *frozen phonon* approximation. One computes the total energy of the system in the equilibrium configuration (that in which the forces acting on the atoms are zero), and then for small displacements of selected atoms (either individually or in the direction of a normal mode, if this is known). The actual value of the atomic displacements (typically a few hundredths of an Å) are parameters chosen by the user. One can either fit the energy vs displacement to a polynomial, and extract a specific vibrational mode,^{6,9} or compute the dynamical matrix by finite differences.⁷ When a few specific modes are all that is needed, only the movement of the atoms involved in those modes is considered. In these methods, it is not possible to isolate the harmonic contributions completely from the anharmonic ones, since finite displacements always involve some anharmonic effects. For this reason, the frequencies obtained in this approach are sometimes referred to as *quasiharmonic*.¹⁰

One can also calculate vibrational properties from constant-temperature molecular-dynamics simulations, for instance by extracting selected frequencies from the velocity-velocity autocorrelation function¹¹ or by using more sophisticated spectral estimators, like the multiple signal classification (MUSIC) algorithm.^{12,13} This is computationally exhausting, since long molecular dynamics runs are required, but potentially very accurate.¹³ This also allows the calculation of frequencies as a function of temperature.

However, a calculation of vibrational frequencies does not necessarily require the actual displacement of the atoms, as in the methods described above. Linear-response theory (in particular through the application of perturbation theory in density-functional theory) was thoroughly used in the past¹⁴ to compute the response of the system to infinitesimal atomic displacements, and from that, the vibrational frequencies in the harmonic approximation. This can be done with only a knowledge of the electronic solution in the equilibrium con-

figuration. The advantage of this approach is that anharmonic effects are eliminated, and that no reference is needed to explicit finite atomic displacements. In addition, this approach allows one to compute phonons with an arbitrary \mathbf{q} vector in crystalline systems, without having to consider a supercell commensurate with the periodicity of the phonon, as is required in the frozen-phonon and molecular-dynamics approaches.

We present a method, based on density-functional perturbation theory (DFPT), to compute vibrational frequencies in the harmonic approximation. We use a basis set of numerical atomic orbitals to expand the electronic wave functions, which makes the method computationally very efficient, and allows us to calculate systems with a large number of atoms. We then apply it to make a systematic study of a number of defect centers in silicon, involving light impurities and their complexes with intrinsic defects (vacancies and self-interstitials). In most cases, a comparison of the calculated and measured vibrational frequencies is very favorable, improving on the results obtained by other approaches.

The outline of this paper is as follows. We first discuss the theoretical method and the model used to describe the defects. Then we compare the vibrational properties obtained for a variety of complexes with experimental data as well as other first-principles calculations in the literature. Finally, we discuss the results.

II. METHODOLOGY

A. Ground-state description

In this work, we use the fully self-consistent *ab initio* code SIESTA.^{15,16} The electronic energy is obtained from density-functional theory (DFT)^{17,18} within the local-density approximation. The exchange-correlation potential is that of Ceperley and Alder¹⁹ as parametrized by Perdew and Zunger.²⁰ Norm-conserving pseudopotentials²¹ in the Kleinman-Bylander form²² are used to remove the core electrons from the calculations.

The valence-electron wave functions are described with numerical linear combinations of atomic orbitals of the Sankey type,²³ but generalized to be arbitrarily complete with the inclusion of multiple-zeta orbitals and polarization states.²⁴ These orbitals are numerical solutions of a free atom with the appropriate pseudopotential, and are strictly zero beyond some cutoff radius. This makes the calculation of the ground-state Kohn-Sham Hamiltonian scale linearly with the number of atoms,^{15,16} allowing calculations in very large systems with a modest computational cost.

In the present work, the basis sets include single-zeta (SZ), double-zeta (DZ), double-zeta plus polarization (DZP), and triple-zeta plus polarization (TZP). A DZP basis includes two sets of s and p 's plus one set of d 's on Si, O, C or B, and two s 's and one set of p 's on H. The radial cutoff of the atomic orbitals was determined as described in Ref. 24, with an energy shift of 0.5 eV, and a split norm of 0.15 for all the species except H, for which the split norm was 0.5. The charge density is projected on a real space grid with an equivalent cutoff of 90–150 Ry to calculate the exchange-correlation and Hartree potentials. The host crystal is repre-

sented by a periodic supercell of 64 host atoms, and the \mathbf{k} -point sampling is reduced to the Γ point. This restriction appears to be quite sufficient for a calculation of vibrational spectra. Tests have been performed for selected defects in a 128-host-atom cell, and the results are within a few wave numbers of those obtained in the 64 host atoms cell.

In order to determine the equilibrium structure of the defects studied, we have relaxed all the atomic coordinates with a conjugate gradient algorithm, reaching a tolerance in the forces of $F_{max} < 0.01$ eV/Å. The dynamical matrix for the whole cell is computed (see below) from this ground state, and its eigenfrequencies and eigenmodes are obtained.

B. Linear-response theory

An implementation of DFPT was developed to compute the electronic response to *infinitesimal* atomic displacements. As is well known from the “ $2n+1$ ” theorem in quantum mechanics,²⁵ the first-order change of the electronic wave function in a perturbative expansion allows the computation of the second-order change in the energies. This implies that only the properties of the unperturbed ground state are needed to obtain the linear response of the system. The extension of this theorem to DFT is that a knowledge of the first-order change in the electronic density variationally determines the second-order change in the energy. In this way, we analytically obtain the dynamical matrix from the gradient of the density relative to atomic displacement and, from this, the vibrational properties, without physically displacing any atom.

Here we briefly describe the key points of our formulation. In the Appendix, additional technicalities are presented. A complete report will be published elsewhere.²⁶ The change in the electronic wave function is obtained by solving the first-order perturbation expansion of the Schrödinger equation (the Sternheimer equation²⁷)

$$\delta\hat{H}\psi_{0,i} + \hat{H}_0\delta\psi_i = \delta\epsilon_i\psi_{0,i} + \epsilon_{0,i}\delta\psi_i, \quad (1)$$

where $\psi_{0,i}$ are the ground-state electronic wave functions and $\delta\psi_i$ the first order perturbation of ψ_i when an atom is displaced (if we consider atom α , this would be $\partial_\alpha\psi_i$). As we expand these wave functions in terms of atomic orbitals ϕ_μ centered at \mathbf{R}_μ ,

$$\psi_{0,i}(\mathbf{r}) = \sum_\mu c_{i\mu}\phi_\mu(\mathbf{r}-\mathbf{R}_\mu), \quad (2)$$

the derivatives can be directly written in terms of the derivatives of the atomic orbitals:

$$\partial_\alpha\psi_i(\mathbf{r}) = \sum_\mu [\partial_\alpha c_{i\mu}\phi_\mu(\mathbf{r}-\mathbf{R}_\mu) + c_{i\mu}\partial_\alpha\phi_\mu(\mathbf{r}-\mathbf{R}_\mu)]. \quad (3)$$

Only the orbitals ϕ_μ centered on atom α appear in the last term which is equal to $-c_{i\mu}\cdot\nabla\phi_\mu(\mathbf{r}-\mathbf{R}_\mu)$. The change in the coefficients, $\partial_\alpha c_{i\mu}$, is obtained from Eq. (1). $\partial\psi_i$ is then used to compute the perturbation in the electronic density

TABLE I. Calculated and measured (Ref. 28) frequencies for free SiH₄, CO, CO₂, and H₂ molecules with various basis sets.

	SZ	SZP	DZ	DZP	TZ	TZP	Expt.
SiH ₄							
T ₂	2045	2064	2160	2153	2173	2159	2191
A ₁	1970	1974	2110	2116	2131	2125	2187
E	800	862	921	929	926	929	975
T ₂	701	772	806	818	817	821	914
H ₂							
A	3619	3670	4194	4185	4193	4191	4161
CO							
A	1681	1823	1885	2088	1945	2183	2170
CO ₂							
A ₁	2118	2355	2235	2277	2224	2394	2349
A ₂	1107	1216	1200	1241	1209	1331	1333
E	478	558	547	583	560	635	667

$$\partial_{\alpha}\rho(\mathbf{r}) = \sum_{i=1}^{occ} [\partial_{\alpha}\psi_i^* \psi_i + \psi_i^* \partial_{\alpha}\psi_i]. \quad (4)$$

This allows a computation of the dynamical matrix, by an explicit derivation of the forces on all the atoms β in the system (the expressions of which can be found in the Appendix, for our approach) with respect to the infinitesimal displacement of one of them (α):

$$(M_{\alpha}M_{\beta})^{1/2}\mathbf{D}_{\alpha\beta} = \frac{\partial^2 E}{\partial\mathbf{R}_{\alpha}\partial\mathbf{R}_{\beta}} = \partial_{\alpha}\mathbf{F}_{\beta}. \quad (5)$$

We remark that only terms up to first order in the electronic wave functions appear in the resulting formulas. Note that only linear effects in the wave function are obtained in this method, which is consistent with the harmonic approximation implicitly assumed in the diagonalization of the dynamical matrix. Thus one expects to obtain high-quality frequencies for the vibrational modes that are harmonic, but the frequencies of modes involving large anharmonic contributions will be less accurate. Although phonons with an arbitrary \mathbf{q} vector can be obtained in the present approach, here we only calculate vibrations which are periodic with the simulation supercell (i.e., $\mathbf{q}=\Gamma$), since we are interested in LVM's.

III. RESULTS

Tests of the method for free SiH₄, CO, CO₂, and H₂ lead to very good agreement with experiment (see Table I). Using an appropriate basis set is essential to reproduce accurate frequencies. In most of the cases a DZ set gives good values, but in some configurations a more complete basis is required. This is particularly true for bending modes. Oxygen ‘‘likes’’ to have polarization orbitals, and thus the frequencies are better when these are included. Note that the vibrational frequencies are more sensitive to the basis set size than the structural properties such as bond lengths. In general, the

largest improvements in the frequencies correspond to going from SZ to DZ, then DZ to DZP, but the TZ basis produce only marginal improvements.

A number of defects containing light impurities in *c*-Si are now considered. These are H at a bond-center (BC) site, H dimers (H₂ and H₂^{*}), the hydrogenated vacancy (VH_{*n*}, *n*=1,2,3,4) and the saturated divacancy V₂H₆, the self-interstitial-hydrogen *I*H₂ complex, the {B,H} pair, substitutional C, interstitial O, and two charge states of the A-center (oxygen-vacancy complex). These embrace a range of Si-*X* bonding configurations, with *X*=H, C, O and B. In most cases, we have tried different basis sets in order to check or improve the accuracy of our calculations when the chemical properties are particularly complex. We show frequencies for the DZ and DZP basis sets. Typically, the calculations of the whole dynamical matrix for each of the systems considered here take around one week of CPU in a 733-MHz Pentium-III processor. Although the diagonalization of the dynamical matrix gives all the (Γ point) modes in the cell, we present here only the stretching and some bending LVM's. We also obtain the eigenvectors which we use to determine the symmetry of the corresponding vibrational modes. Our results are compared with available experimental data, and with theoretical frequencies obtained by other authors using first-principles DFT.

A. H_{BC}, H₂, and H₂^{*}

At the BC site,²⁹ hydrogen exists in the +1 and 0 charge states. In the latter case, the odd electron does not participate in the bonding but resides in a nonbonding orbital primarily localized on the two Si atoms adjacent to the proton. Chemically, this is a three-center, two-electron bond, very much like the type of H bonding occurring in boron hydrides. The bond is somewhat compressed because optimal relaxation (no Si second-nearest neighbors) would likely result in a longer Si-H-Si bond and a frequency lower than observed. This suggests that as H moves along the trigonal axis, it tends to form something like Si . . . H-Si, then Si-H-Si, then Si-H . . . Si, a process which is highly anharmonic. The calculated frequency is given in Table II.

Raman⁴⁰ and IR^{33,41} measurements of H₂ in silicon reveal a considerable softening of the stretching mode with respect to the frequency of H₂ in the gas phase. A number of calculations (for a review, see Ref. 39) found the molecule to be stable at the tetrahedral interstitial (*T*) site. The electron affinity of the Si atoms surrounding H₂ is at least partly responsible for a small charge transfer from H₂ to its Si neighbors, which results in a weakening of the H-H bond. Even though the H-H stretch mode is not expected to be fully harmonic, our calculated frequency is close to the experimental one (Table II). Note that the errors relative to experiment in the D₂ and HD frequencies are very different than the error in the H₂ frequency. This is also a clear feature of these frequencies when they are calculated dynamically from the *v-v* autocorrelation function.⁴²

The trigonal H₂^{*} defect⁸ consists of one hydrogen atom close to the antibonding (AB) site, and the other near the BC site (see Fig. 1). The two H atoms are inequivalent. The

TABLE II. Calculated and measured frequencies for H_{BC} (our calculation is spin polarized for H_{BC}^0 and spin averaged for H_{BC}^+), H_2 in the $\langle 100 \rangle$ alignment, and $H_2^* = H_{BC}H_{AB}$. A DZ basis was used for all these complexes. The errors relative to experimental values are in parentheses. Were H_2 a classical dumbbell, its wag modes would be at 731 and 860 cm^{-1} (see the discussion in Ref. 39).

	Expt.	This work	Other authors		
H_{BC}^+	1998 ^a	1891(−5%)	H_{BC} 2203 ^b (+10%)	2210 ^c (+11%)	
H_{BC}^0	—	1813	1768 ^b	1945 ^c	
H_2 in Si					
H_2	3618 ^d	3549(−2%)	3607 ^e (+0%)	3396 ^f (−6%)	3260 ^g (−9%)
DH	3265 ^d	3081(−6%)	3129 ^e (−4%)		
D_2	2643 ^d	2511(−5%)	2559 ^e (−3%)		
H_2^*	2062 ^g	2135(+3%)	2164 ^g (+5%)	2100 ^h (+2%)	1945 ⁱ (−5%)
	1838 ^g	1750(−5%)	1844 ^g (+0%)	1500 ^h (+18%)	1677 ⁱ (−9%)
	817 ^g	843/839(+3%)	1002 ^g (+22%)	711 ⁱ (−13%)	

^aReference 30.

^bReference 31.

^cReference 32.

^dReference 33.

^eReference 34.

^fReference 35.

^gReference 36.

^hReference 37.

ⁱReference 38.

Si- H_{AB} bond length is slightly longer than the Si- H_{BC} one (we obtain 1.580 and 1.510 Å, respectively) which gives rise to different stretch frequencies for the two atoms: 2135 cm^{-1} for H_{BC} and 1750 cm^{-1} for H_{AB} . We also obtain two degenerate wagging modes, associated with the H_{BC} atom, at 560 cm^{-1} , and two wagging modes with 839 and 843 cm^{-1} , related to H_{AB} . The latter should be degenerate, but small inaccuracies in the atomic relaxations render them at slightly different frequencies.

B. Hydrogen and native defects

A considerable number of IR and Raman lines are related to H-intrinsic defect complexes. It has been noted^{43,44} that vibrational modes above 2000 cm^{-1} are mainly related to H

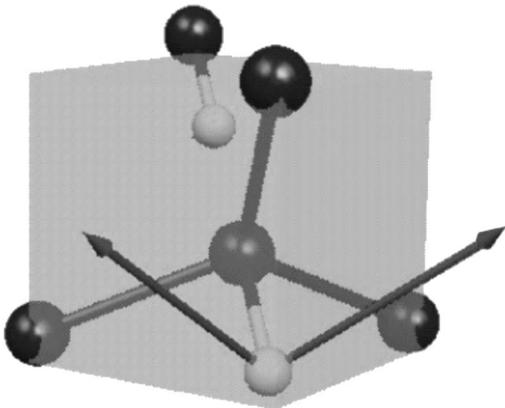


FIG. 1. Calculated structure of a H_2^* complex in silicon. Dark spheres are Si atoms, white spheres are H. The two perpendicular arrows represent the H_{AB} wag eigenmodes at 842 cm^{-1} . The twofold-degenerate wagging mode for H_{BC} is found at 560 cm^{-1} .

in vacancies, while those lines below 2000 cm^{-1} are predominant for H-self-interstitial systems or H at AB sites. A large number of geometrical configurations may lead to very similar vibrational lines, making it difficult to identify these defects unambiguously. As noted by other groups,^{2,45–47} the stretching frequencies in VH_n ($n=1,2,3,4$) systems increases with n due to the repulsive H-H interaction. Thus, the highest IR line is that of VH_4 . Si-H bonds point toward the center of the vacancy along the trigonal axes.

In our calculations (Table III), VH has monoclinic symmetry, and the H oscillates parallel to the $\langle 111 \rangle$ direction. In orthorhombic VH_2 , two equivalent H's have stretching modes along the $\langle 100 \rangle$ and $\langle 001 \rangle$ directions. The frequencies for these modes are 2121 and 2144 cm^{-1} respectively. VH_3 has C_{3v} symmetry. The A singlet involves the movement of three H atoms toward the vacancy, while in the twofold-degenerate E mode one of the atoms moves in opposition. VH_4 has T_d symmetry. In addition to the threefold-degenerate T_2 mode at 2205, we obtain an IR-inactive singlet A_1 mode at 2265 cm^{-1} .

The vibrational modes of V_2H_6 are almost identical to those of VH_3 : The fully saturated divacancy behaves very much like two weakly coupled VH_3 complexes. The A_2 singlet at 2176 cm^{-1} induces a dipole along the $\langle 111 \rangle$ direction. In addition to this mode and the IR-active E doublet, we obtain two IR-inactive modes at 2186 and 2134 cm^{-1} .

The IH_2 complex⁵⁰ has two equivalent and weakly coupled hydrogen atoms, which yields two very similar stretching frequencies. Uniaxial stress measurements show that the two hydrogen atoms are equivalent. Our relaxed structure has an almost C_{2v} symmetry, with the A mode higher than the B mode, confirming early results.⁵⁰ The deviation from perfect symmetry is due to the finite tolerance

TABLE III. Calculated and measured frequencies for stretching modes in VH_n ($n=1,2,3,4$) and V_2H_6 . The error relative to experiment is in parentheses. Our frequencies were obtained with a DZP basis. The measured values for the VH_2D , VHD_2 and VD_3 , as published in Ref. 44, are now believed to belong to a divacancy complex (Ref. 49) and are therefore not listed here.

	Expt. ^a	This work	Other authors ^b		Expt. ^a	This work	Other authors ^b
		VH				VH ₄	
A'	2038	1971(-3%)	2248(+10%)	A ₁	2257 ^c	2265(+0%)	2404(+6%)
		VD		T ₂	2222	2205(-1%)	2319(+4%)
A'	1507	1418(-6%)	1613(+7%)			VH ₃ D	
		VH ₂		A ₁	2250	2251(+0%)	2384(+6%)
A ₁	2144	2163(+1%)	2316(+7%)	E	2224	2205(-1%)	2319(+4%)
B ₁	2121	2132(+1%)	2267(+7%)	A ₁	1620	1594(-2%)	1677(+3%)
		VHD				VH ₂ D ₂	
A'	2134	2135(-0%)	2292(+7%)	A ₁	2244	2235(-0%)	2364(+5%)
A'	1555	1551(-0%)	1641(+5%)	B ₁	2225	2204(-1%)	2319(+4%)
		VD ₂		A ₁	1628	1603(-1%)	1690(+4%)
A ₁	1564	1552(-1%)	1658(+6%)	B ₂	1615	1585(-2%)	1663(+3%)
B ₁	1547	1532(-0%)	1625(+5%)			VHD ₃	
		VH ₃		A ₁	2236	2221(-1%)	2342(+5%)
A ₁	2185	2158(-1%)	2318(+6%)	A ₁	1636	1613(-1%)	1705(+4%)
E	2155	2100(-2%)	2256(+5%)	E	1616	1584(-2%)	1664(+4%)
		VH ₂ D				VD ₄	
A'		2140	2298	A ₁	no-IR	1623	1721
A''		2101	2256	T ₂	1617	1584(-2%)	1664(+3%)
A'		1520	1632			V ₂ H ₆	
		VHD ₂				V ₂ H ₆	
A'		2121	2277	A ₁	2190 ^c	2186(-0%)	-
A'		1534	1646	A ₂	2191	2176(-0%)	-
A''		1509	1619	E	2166 ^c	2143(-1%)	-
		VD ₃		E	2165	2134(-1%)	-
A ₁		1547	1661				
E		1510	1619				

^aReference 44.

^bReference 45.

^cReference 48.

in the geometry optimization. This deviation is seen when comparing the *IHD* and *IDH* complexes: they should be identical, but we find their frequencies to be off by 2 cm^{-1} . Note that we reproduce the correct ordering for the bending modes of *IH*₂ at 737 and 732 cm^{-1} (Table IV).

C. Oxygen, carbon, and boron in silicon

Oxygen is a well-known impurity which is especially important in Czochralski-grown Si, and a considerable amount of effort was focused in understanding its properties.⁵¹ We have computed the LVM frequencies for interstitial oxygen (*O_i*) and two charge states of the vacancy-oxygen complex (*A* center). The results are in Table V. Frequencies for *O_i* were computed with the oxygen placed at the BC site, where the probability of finding this delocalized atom is at a maximum, and the classical harmonic potential can better describe the local modes. The IR-active *A*_{2_u mode corresponds to the asymmetric-stretching mode, while the *A*_{1_g is the symmetric one. The *E_u* mode involves the movement of nearest}}

silicon atoms with no participation of the oxygen.⁵² Finally, Table VI shows the triply degenerate mode of substitutional carbon as well as the LVM's associated with a {B,H} complex.²

IV. CONCLUSIONS

We have presented a development of DFPT, using localized atomic wave functions as a basis set, and applied it to the study of LVM's for light impurities in silicon. In contrast to other methods, the dynamical matrix is computed analytically without actually displacing any atom from its equilibrium position. The calculations are based on the ground-state density matrix, as computed with the SIESTA package.

Tests of the method for free molecules (*SiH₄*, *H₂*, *CO*, and *CO₂*) show that this approach is highly accurate in situations where the anharmonic contributions are small. Note that the frequencies are obtained at *T*=0 K, while experimental data are obtained at low, but nonzero, temperatures.

We have used a variety of basis set sizes to describe the

TABLE IV. Calculated frequencies with a DZ basis set compared with experimental and other theoretical results for IH_2 . The error relative to experiment is in parenthesis.

	Expt. ^a	This work			Other authors			Expt. ^a	This work			Other authors		
		IH_2							ID_2					
A	1989	2007	(+1%)	2107 ^b	(+6%)	2145 ^a	(+8%)	1448	1440	(-1%)	1510 ^b	(+4%)	1540 ^a	(+6%)
B	1986	2004	(+1%)	2106 ^b	(+6%)	2143 ^a	(+8%)	1446	1438	(-1%)	1508 ^b	(+4%)	1539 ^a	(+6%)
B	748	737	(-1%)			(A) 775 ^a	(+3%)		609				590 ^a	
A	743	733	(-1%)			(B) 768 ^a	(+3%)		601				583 ^a	
A		716				(B) 736 ^a			566				564 ^a	
B		711				(A) 717 ^a			562				555 ^a	
IHD/IDH														
	Expt. ^a	This work						Other authors						
	1988	2005/2007 (+1%)						2106 ^b (+6%) 2144 ^a (+8%)						
	1447	1440/1438 (-1%)						1509 ^b (+3%) 1540 ^a (+6%)						
	746	733/736 (-2%)						771 ^a (+3%)						
		714/714						727 ^a						

^aReference 50.^bReference 45.

electronic wave functions. In most cases, a DZ basis is quite sufficient to obtain accurate atomic structures and vibrational frequencies. Larger basis sets such as DZP improve the frequencies in situations that involve more complex chemical bondings. The defects included here are H_{BC} , H_2 , H_2^* , VH_n (with $n = 1, 2, 3, 4$), V_2H_6 , IH_2 , the $\{B, H\}$ pair, substitutional C, interstitial O, and two charge states of the A center. These defects involve a wide range of bonding configurations.

The average error relative to experiment of the ~ 60 calculated modes is about 2%. In situations where large anharmonic contributions are present, the accuracy of the method decreases somewhat (5–6%). This occurs, for example, when H is close to a BC position. However, in most cases the calculated frequencies are in remarkable agreement (0–2%) with experimental data, implying that this perturbative approach is totally justified and that the ground-state density matrix calculated with SIESTA is very reliable.

TABLE V. Calculated and measured LVM's for interstitial O (O_i) and two charge states of the A center (VO^0 and VO^-). For $VO^{(0/-)}$ a DZP basis was used for O and its Si nearest-neighbors, and a DZ basis for the other Si atoms. For O_i , a DZP basis was used for all the atoms in the cell. The symmetry of O_i structure is shown above the frequencies.

	Expt. ^a	This work			Other authors ^b			Other authors ^c			
		D_{3d}						C_2			
		A_{2u}	1136	1131	(-0%)	1184	(+4%)	1108	(-2%)	1098	(-3%)
O_i		A_{1g}	618	607	(-2%)	619	(+0%)	621	(+0%)	630	(+2%)
		E_u	518	538	(+4%)	519	(+0%)	518	(+0%)		
VO^0		B_1	836	861	(+3%)			839 ^a	(+0%)	843	(+1%)
		A_1	534	546	(+2%)			548 ^a	(+3%)	540	(+1%)
VO^-		B_1	885	897	(+1%)			872 ^a	(-1%)	850	(-4%)
		A_1	545	558	(+2%)			532 ^a	(-2%)	539	(-1%)

^aReference 53 for O_i Ref. 54 for $VO^{(0/-)}$.^bReference 55.^cReference 56.

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APPENDIX: TECHNICALITIES

The unperturbed electronic density $\rho^0(\mathbf{r})$ is written in terms of the density matrix $\rho_{\mu\nu}^0$,

TABLE VI. Calculated and measured frequencies for substitutional C and the {B,H} pair in Si. A DZP basis was used for C and its Si nearest-neighbors, and DZ for the other atoms. For the {B,H} pair, a DZ basis was used for all the atoms.

	Expt.	This work		Other authors	
C _s	T _d	607 ^a	631 (+4%)	662 ^b	(+9%)
	A	1903 ^c	1958 (+3%)	1830 ^d	(-4%)
{B,H}				1880 ^e	(-1%)
	E	652	695 (+6%)		

^aReference 57.

^bReference 58.

^cReference 59.

^dReference 61.

^eReference 62.

^fReference 60.

$$\begin{aligned} \rho^0(\mathbf{r}) &= \sum_i n_i |\psi_i^0(\mathbf{r})|^2 = \sum_{\mu,\nu} \left(\sum_i n_i c_{i\mu}^* c_{i\nu} \right) \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}) \\ &= \sum_{\mu,\nu} \rho_{\mu\nu}^0 \phi_\mu^*(\mathbf{r}) \phi_\nu(\mathbf{r}), \end{aligned} \quad (\text{A1})$$

where n_i is the occupation of state i , and μ, ν loop over the orbitals in the basis set.

When we consider a perturbed system, we can express the change in the electronic density in a similar way, defining a density matrix $\partial_\alpha \rho_{\mu\nu}$:

$$\begin{aligned} \partial_\alpha \rho(\mathbf{r}) &= \sum_{\mu,\nu} \partial_\alpha \rho_{\mu\nu} \cdot \phi_\mu^*(\mathbf{r}) \cdot \phi_\nu(\mathbf{r}) \\ &+ \sum_{\mu\nu} \rho_{\mu\nu}^0 \cdot [\partial_\alpha \phi_\mu^*(\mathbf{r}) \cdot \phi_\nu(\mathbf{r}) + \phi_\mu^*(\mathbf{r}) \cdot \partial_\alpha \phi_\nu(\mathbf{r})]. \end{aligned} \quad (\text{A2})$$

The matrix $\partial_\alpha \rho_{\mu\nu}$ involves derivatives of the coefficients $c_{i\mu}$, which are obtained from the solution of the Eq. (1). Its final expression²⁶ is

$$\begin{aligned} \partial_\alpha \rho_{\mu\nu} &= \sum_i n_i \sum_j c_{i\mu}^* \sum_{\mu',\nu'} c_{j\mu'}^* \frac{\partial_\alpha H_{\mu'\nu'} - \epsilon_i \partial S_{\mu'\nu'}}{\epsilon_i - \epsilon_j} c_{i\nu'} c_{j\nu} \\ &+ \sum_i n_i \sum_j c_{j\mu}^* \sum_{\mu',\nu'} c_{i\nu'}^* \frac{\partial_\alpha H_{\nu'\mu'} - \epsilon_i \partial S_{\nu'\mu'}}{\epsilon_i - \epsilon_j} c_{j\mu'} c_{i\nu} \\ &+ \sum_i n_i \partial_\alpha \epsilon_i 2 c_{i\mu}^* c_{i\nu} + \sum_i \partial_\alpha n_i \epsilon_i 2 c_{i\mu}^* c_{i\nu}, \end{aligned} \quad (\text{A3})$$

where $\partial_\alpha H_{\mu\nu}$ and $\partial_\alpha S_{\mu\nu}$ denote the change in the Hamiltonian and overlap matrices $H_{\mu\nu} = \langle \phi_\mu | \hat{H} | \phi_\nu \rangle$ and $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$. Once the change in the density matrix $\partial_\alpha \rho_{\mu\nu}$ is known, we derive the expression of the forces in SIESTA with respect to atomic displacement (Ref. 16):

$$\begin{aligned} \mathbf{F}_\beta &= - \frac{\partial E}{\partial \mathbf{R}_\beta} = - \sum_{\mu\nu} \rho_{\mu\nu} \frac{\partial H_{\mu\nu}^0}{\partial \mathbf{R}_\beta} + \sum_{\mu\nu} E_{\mu\nu} \frac{\partial S_{\mu\nu}^0}{\partial \mathbf{R}_\beta} \\ &- \int \frac{\partial V^{NA}(\mathbf{r})}{\partial \mathbf{R}_\beta} \delta \rho(\mathbf{r}) d\mathbf{r} - \frac{1}{8\pi} \sum_{jk} \frac{\partial}{\partial \mathbf{R}_\beta} \\ &\times \int V^{NA}(\mathbf{r} - \mathbf{R}_{jk}) \nabla V^{NA}(\mathbf{r}) d\mathbf{r} + 2 \sum_{\mu} \rho_{\mu}^0 \left\langle \frac{\partial \phi_{\mu}}{\partial \mathbf{R}_\beta} \right| V_H^\delta \\ &+ V^{NA} \left| \phi_{\mu} \right\rangle - 2 \sum_{\mu\nu} \rho_{\mu\nu} \left\langle \frac{\partial \phi_{\mu}}{\partial \mathbf{R}_\beta} \right| V_H^\delta + V_{xc} \left| \phi_{\nu} \right\rangle. \end{aligned} \quad (\text{A4})$$

Here $H_{\mu\nu}^0$ stands for the non-self-consistent contribution of the Hamiltonian (kinetic plus nonlocal pseudopotential terms); the matrix $E_{\mu\nu} = \sum_i \epsilon_i c_{i\mu}^* c_{i\nu}$ is defined in a similar way to $\rho_{\mu\nu}$, V^{NA} is the screened neutral-atom potential; $\delta \rho(\mathbf{r})$ is the difference $\rho(\mathbf{r}) - \rho^{atom}(\mathbf{r})$, where ρ^{atom} is a sum of localized atomic densities; V_H^δ is the Hartree potential of $\delta \rho$; and V_{xc} is the exchange-correlation potential.

Note that, in $\partial_\alpha \mathbf{F}_\beta = - \partial^2 E / \partial_\alpha \partial_\beta$, just first-order derivatives of $\rho_{\mu\nu}$ will appear, and that the knowledge of $\partial_\alpha \rho_{\mu\nu}$ would enable the computation of a whole row of the dynamical matrix. More details of the computation of these matrix elements will be published elsewhere.²⁶

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