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Shallow-acceptor spectral-line fine structure in germanium

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A controlled-accuracy, high-resolution energy spectrum of the 4×4 Kohn-Luttinger Hamiltonian with a screened Coulomb impurity potential has been obtained. The calculated and measured spectra were adjusted using selected line positions. An identification of the boron spectrum reveals a complex structure for most of the lines. The identification yields the splittings in the multiplets and chemical shifts of the odd-parity excited states. An estimated splitting in the C triplet of 53 μeV is in fair agreement with the reported separation for Ge(B), Ge(Al), and Ge(In). New data on the spectroscopic values of the ground-state binding energies for nine experimentally studied acceptors are presented.

I. INTRODUCTION

The study of bulk-semiconductor shallow acceptor (SA) spectra has been an active area of exploration for more than three decades. By now, detailed experimental acceptor spectra in ultrapure germanium (net acceptor concentrations of 10^9-10^{12} cm^{-3}) are available, providing a basis for systematic theoretical research. Although the main features of the acceptor problem are well explained in the framework of the effective-mass theory (EMT) (Refs. 1 and 2) and the spherical model[3,4] which have led to an improved understanding of many properties of SA's, problems of interpretation of far-infrared absorption spectroscopy (FIRAS) (Ref. 5) and photothermal ionization spectroscopy (PTIS) (Refs. 6–9) data necessitated corrections in the model. The refined spherical model was developed to describe more accurately the Γ_8^+ valence-band warping by adding to the envelope-function expansion terms with larger values of orbital momentum L. It also includes q-dependent screening,[10] a short-range potential,[11] and coupling to the split-off Γ_7^+ valence band. It should be kept in mind that in the SA-state calculation there is no estimation of the truncation errors of the envelope-function expansion in a series of angular functions,[11–13] and further, there is no estimation of inaccuracies induced by a variational solution of the radial differential equations for the r-dependent coefficients of this series.[3,4,10–13]

The methods of singular boundary problem numerical analysis for ordinary differential equations (ODEs) (Refs. 14–16) have turned out to be a useful technique in investigation of the acceptor problem.[17–20] These studies showed that the high-order envelope-function angular basis expansion (HOABE) (Ref. 17) and numerical segregation of bounded solutions (NSOBS) for ODE sets dealing with local transfer of boundary conditions from singular points[15,16] and variants of the orthogonal differential marching method,[14] allow us to obtain 60 SA energy levels (EL's) in Ge for low orders of the ODE matrices with an accuracy of the eigenvalue calculation of ~ 0.5 μeV. The accuracy was evaluated from analytical solutions for Γ_6^+, Γ_7^+ states with 2×2 ODE matrices.

In this paper, we will extend these computations to the comprehensive calculation of SA states in Ge. The implications of this method in a spectral identification are illustrated with an example: B in Ge. The results of the computations also indicate that HOABE and NSOBS methods give rise to significant lowering of EL's of SA's in Ge as compared to the earlier EMT calculations in the spherical model for the 4×4 Kohn-Luttinger Hamiltonian with a screened Coulomb impurity potential, both without introducing q-dependent dielectric screening and taking into account the decoupled Γ_7^+ split-off valence band. Comparison of our calculations and previous EMT calculations of the lowest 25 EL's for the same problem shows that the differences lie between 3.65% ($1\Gamma_7^-$) and 19.3% ($1\Gamma_6^-$) (the spherical model with cubic contributions, Ref. 4), -41.8% ($1\Gamma_7^+$) and 11.0% ($7\Gamma_8^+$) (the same model, Ref. 9), and -5.18% ($3\Gamma_7^-$) and 9.24% ($7\Gamma_8^+$) (the spherical model with cubic contributions and ODE set solved by the finite-element method, Ref. 21; the estimations were obtained by linear extrapolation to $\mu=0.7638$ and $\delta=0.1084$ for Ge).

II. EMT-EQUATION-SOLVING ALGORITHM

The underlying idea of this approach is an implementation in a standard SA-state calculation of (i) the arbitrary order cubic basis algorithm and (ii) the singular boundary problem numerical analysis for radial ODE sets. No correction for the potential in the central cell was made and the split-off Γ_7^+ valence band was not taken into account. As for the first approximation, the influence the central cell and its nearest neighbors have on energy states is considered a generation of the EL chemical shifts. The second approximation is justified at the first stage of the computation because of the large value of spin-orbit valence-band splitting $\Delta_0=290$ meV in Ge, as compared to the scale of SA excited-state energy differences ~ 1 meV. The L-S-type coupling scheme of the orbital momentum L to the pseudospin $S=\frac{3}{2}$ was used.[22] The nonvariational NSOBS method in these calculations replaced the variational solution of the sets of ODE's in previous calculations.[3,4,10–13]

If we combine the Clebsch-Gordan coefficient technique relevant to L-S coupling and the finite-rotation ma-

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trices for elements of the group O',[23] we obtain the closed expressions for cubic harmonics of indices l,j,m of the representations $\alpha=\Gamma_i^{\pm}$, $i=6,7,8$ in the form of the decomposition in series of four spinors of the angular momentum eigenfunctions Ψ_{ljm}:

$$\varphi_{ljm}^{(\alpha)}=\sum_{m'=-j}^{j} A_{m'm}^{(\alpha,j)}\Psi_{ljm'} ,$$

$$A_{m'm}^{(\Gamma_6,j)}=\tfrac{1}{3}\left[\delta_{m'm}+2\sqrt{2}d_{m'm}^{(j)}\left[\frac{\pi}{2}\right]\delta_{m',m+4s}\right] ,$$

$$m=\pm|\pm\tfrac{1}{2}+4t| , \quad s,t=0,\pm 1,\pm 2,\ldots ,$$

$$A_{m'm}^{(\Gamma_7,j)}=\tfrac{1}{3}\left[\delta_{m'm}-2\sqrt{2}d_{m'm}^{(j)}\left[\frac{\pi}{2}\right]\delta_{m',m+4s}\right] ,$$

$$m=\pm|\pm\tfrac{3}{2}+4t| , \quad s,t=0,\pm 1,\pm 2,\ldots , \tag{1}$$

$$A_{m'm_1}^{(\Gamma_8,j)}=\tfrac{2}{3}\left[\delta_{m'm_1}-\sqrt{2}d_{m'm_1}^{(j)}\left[\frac{\pi}{2}\right]\delta_{m',m_1+4s}\right] ,$$

$$m_1=\pm|\pm\tfrac{1}{2}+4t| , \quad s,t=0,\pm 1,\pm 2,\ldots ,$$

$$A_{m'm_2}^{(\Gamma_8,j)}=\tfrac{2}{3}\left[\delta_{m'm_2}+\sqrt{2}d_{m'm_2}^{(j)}\left[\frac{\pi}{2}\right]\delta_{m',m_2+4s}\right] ,$$

$$m_2=\pm|\pm\tfrac{3}{2}+4t| , \quad s,t=0,\pm 1,\pm 2,\ldots ,$$

where the functions $d_{m'm}^{(j)}(\beta)$ are given in Ref. 23. Group-theoretical methods[23] yield ljm sets for the irreducible representations.

The envelope-wave function (WF) is a matrix product of a $4\times N$ matrix of angular part $\varphi_{ljm}^{(\alpha)}$ and the N column of radial part $R=\{R_{n,ljm}^{(\alpha)}\}$ of the WF; the order of the matrices of a radial ODE set is equal to N.

The boundary problem for a radial ODE set is written

$$a_1 r^2 R''+a_2 rR'+(a_3+a_4 r+Ea_5 r^2)R=0 , \quad 0<r<\infty , \tag{2a}$$

$$R(0) \text{ is bounded} , \tag{2b}$$

$$\lim_{r\to\infty} R(r)=0 , \tag{2c}$$

where a_q, $q=1,\ldots,5$, are constant $N\times N$ matrices. Their elements depend on the expansion coefficients (1) in a complicated way.

There are three steps involved in solving Eqs. (2).

(i) The transfer of the boundary condition (2b) from the singular point $r=0$ to the neighboring point r_0.[14,15] In the form of the first-order equation for $2N$ vector z,

$$rz'=A(r,E)z , \quad z=\begin{bmatrix} R \\ rR' \end{bmatrix} ,$$

$$A(r,E)=A_0+A_1 r+A_2 r^2 ,$$

$$A_0=\begin{bmatrix} 0 & I \\ -C & I-B \end{bmatrix} , \quad A_1=\begin{bmatrix} 0 & 0 \\ -D & 0 \end{bmatrix} , \tag{3}$$

$$A_2=\begin{bmatrix} 0 & 0 \\ -EF & 0 \end{bmatrix} ,$$

$$B=a_1^{-1}a_2 , \quad C=a_1^{-1}a_3 , \quad D=a_1^{-1}a_4 , \quad F=a_1^{-1}a_5 .$$

(I is the unit $N\times N$ matrix), the solutions of Eq. (2a), which satisfy the boundary condition $\lim_{r\to 0} z(r)=0$, form an N-dimensional linear subspace $\mathbb{M}^{(N)}(r)$ in the (z^-,z^+) space. This subspace for sufficiently small r can be specified in the form

$$z^-(r)=\alpha(r)z^+(r) , \quad z=\begin{bmatrix} z^- \\ z^+ \end{bmatrix} , \quad r\le r_1 \ll 1 ,$$

where $N\times N$ matrix $\alpha(r)=\sum_{j=1}^{\infty}\alpha_j r^j$ is the solution of the singular Cauchy problem

$$r\alpha'=A_0^-\alpha-\alpha A_0^+ +V_{11}\alpha-\alpha V_{22}-\alpha V_{21}\alpha+V_{12} , \quad 0<r\le r_1 , \tag{4a}$$

$$V(r,E)=A(r,E)-A_0=\begin{bmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{bmatrix} , \quad V_{ik}=\sum_{j=1}^{2} V_{ik}^{(j)}r^j , \quad i,k=1,2 , \tag{4b}$$

$$\lim_{r\to 0}\alpha(r)=0 , \tag{4c}$$

where $V_{ik}^{(j)}$ can be expressed in terms of matrices B, C, D, and F. A substitution of the series for $\alpha(r)$ into Eq. (4a) yields α_j in form of the recurrence relations.

(ii) The transfer of boundary condition (2c) to point $r_\infty \gg 1$ by using the equivalence[16,17]

$$R'=\beta(r_\infty)R . \tag{5}$$

The equation for the matrix $\beta\approx\sum_{j=0}^{\infty}\beta_j(1/r^j)$, $r\to\infty$ (asymptotic series) is derived:

$$\beta'+\beta^2+\frac{1}{r}B\beta+\frac{1}{r^2}(C+Dr+EFr^2)=0 . \tag{6}$$

We find the recurrence relations for β_j by substituting an expansion of β into Eq. (6).

With the benefit of the results (i) and (ii), the boundary problem (2) is reduced to an equivalent problem without singularities over the finite interval $[r_0,r_\infty]$:

$$rz'-A(r,E)z=0 , \quad r_0\le r\le r_\infty , \tag{7a}$$

$$\tilde{\Psi}(r_0)z(r_0)=0 , \quad \Psi(r_0)=\begin{bmatrix} I \\ -\tilde{\alpha} \end{bmatrix} , \tag{7b}$$

$$\tilde{\Psi}(r_\infty)z(r_\infty)=0 , \quad \Psi(r_\infty)=\begin{bmatrix} \tilde{\beta} \\ -I \end{bmatrix} . \tag{7c}$$

(iii) The evaluation of the E eigenvalues of problem (7) using a version of the stable differential marching method (Refs. 14 and 17). We solve problem (7) by "shooting" for parameter E: for a fixed value of $E<0$, we transfer the boundary conditions (7b) and (7c) from points r_0 and r_∞ to point $\hat{r}\in[r_0,r_\infty]$. The eigenvalues of E are sought from the condition of nontrivial compatibility of linear algebraic equations at point $\hat{r}$.

The boundary condition (7b) [analogously, (7c)] segregates in 2N-dimensional space of the solutions of Eq. (7a) N-dimensional linear subspace $\mathbb{M}^{N}(r)$, which can be represented for all $r\in[r_0,r_\infty]$ in the form $\tilde{\Psi}(r)z(r)=0$.

The $2N \times N$ matrix Ψ then defines the $\mathbb{M}^N(r)$ and is a solution of the equation

$$r\Psi' + \tilde{A}\Psi - \Psi(\tilde{\Psi}\Psi)^{-1}\tilde{\Psi}\tilde{A}\Psi = 0 \ , \quad r_0 \le r \le r_\infty \ . \qquad (8)$$

An application of a two-sided marching method of Ref. 14 gives the solution of the $2N$ column $z(r)$.

III. RESULTS AND DISCUSSION

The Γ_8^+ valence-band parameters used were $\gamma_1 = 13.38$, $\gamma_2 = 4.24$, and $\gamma_3 = 5.69$,[24] and the static dielectric constant was $\varepsilon_\infty = 15.29$. The value of ε_∞ was obtained at 4.2 K in the wavelength region 0.25–2.5 mm.[25] The unit of energy was

$$\mathrm{Ry}^* = \frac{m_0 e^4}{2\hbar^2 \gamma_1 \varepsilon_\infty^2} = 4.355 \ \mathrm{meV} \ .$$

An absolute accuracy of EL calculation for every order N was 10^{-4}–10^{-5}. The EL's depend on the parameters $\gamma_2/\gamma_1 = 0.3169$ and $\gamma_3/\gamma_1 = 0.4253$, which may be obtained from experimental data, again with an absolute accuracy of 10^{-4}.

The dependence of EL's on the number of terms N in the truncated series of the envelope function was studied. The upper bound for errors was estimated as the differences between the energy eigenvalues, E, calculated at two neighboring values of N corresponding to $L_{\max}$ and $L_{\max} - 2$, where $L_{\max}$ is the maximum value of L in the envelope-function series. $L_{\max} = 8$ was used for even states and $L_{\max} = 7$ for odd states. The corresponding couples of N are 9 and 15 for Γ_6^+ and Γ_7^+, 19 and 30 for Γ_8^+, 7 and 12 for Γ_6^- and Γ_7^-, and 14 and 24 for Γ_8^-.

Table I shows, as an example, the dependence of the binding energies $E_B = -E$ for states Γ_8^+ and Γ_7^- on order N of the ODE matrices for the ten lowest EL's. The following conclusions may be drawn. (i) All compared EL's calculated for larger values of N have a greater E_B than EL's calculated for smaller values of N. (ii) Proceeding from lower to higher N, new EL's appear in the energy spectrum. (iii) The newly appearing EL's for $N_{i+1} > N_i$ have a lower E_B than the new EL's for N_i ($i = 1, 2, 3$ for even states and $i = 1, 2$ for odd states). (iv) A convergence of EL values is observed with increasing N.

In Table II, we have summarized the E_B values of EL's for the six types of symmetry calculated in the highest and next-to-highest approximations in the energy region corresponding to the final states of the reported transitions: G, E, D, C, a, B, b, $A4 - A1$, $I10 - I1$, and included the results of the variational EL calculation in the spherical model. We used the results of Ref. 9 instead of Refs. 3 and 4 because calculations in Ref. 9 are more thorough and were performed with the same valence-band parameters and static dielectric constant as were used here.

As can be seen from Tables I and II, the numbers of EL's up to $10\Gamma_6^+$, $7\Gamma_7^+$, $18\Gamma_8^+$, $5\Gamma_6^-$, $6\Gamma_7^-$, and $17\Gamma_8^-$ are coincident at least for highest- and next-to-highest-order N. These EL's are the controlled-accuracy calculated levels. The upper bounds of their inaccuracies are estimated to be the differences in highest and next-to-highest orders N:$E_B(N_4) - E_B(N_3)$ for even states and $E_B(N_3) - E_B(N_2)$ for odd states. The calculation inaccuracies of the EL's which do not belong to this group are considered to be equal to the E_B differences of compared EL's, such as $12\Gamma_6^+$, or in the case of the absence of the EL in the previous approximation, equal to the differences for low-lying EL's calculated in both approximations, for example, $7\Gamma_7^-$. The upper bounds of EL calculation inaccuracies are equal: 1.9 μeV ($13\Gamma_6^+$)–13.2 μeV ($1\Gamma_6^+$), 6.1 μeV ($10\Gamma_7^+$)–29.6 μeV ($5\Gamma_7^+$), 2.7 μeV ($4\Gamma_8^+$)–14.4 μeV ($3\Gamma_8^+$), 2.1 μeV ($3\Gamma_6^-$)–20.2 μeV ($5\Gamma_6^-$), 11.2 μeV ($18\Gamma_7^-$)–26.2 μeV ($1\Gamma_7^-$), and 7.5 μeV ($10\Gamma_8^-$)–36.0 μeV ($9\Gamma_8^-$) (Table II). It can be seen that there is *a significant lowering* of all the $\Gamma_8^\pm$, $1\Gamma_7^-$, $2\Gamma_7^-$, and $4\Gamma_7^-$, and *a raising* of the $3\Gamma_7^-$, and $5\Gamma_7^-$, and most of the $\Gamma_6^\pm$, and Γ_7^+ EL's calculated here as compared to the spherical model. This difference is due to an accurate consideration of the Γ_8^+ valence-band warping in our approach. The differences are of the order of hundreds of μeV and are much larger than basis-set truncation errors ~2–36 μeV. The EL's, for instance, of Γ_8^- states have been calculated to $46\Gamma_8^-$. The resolution of the $35\Gamma_8^-$ ($E_B = 0.2637$ meV) and $36\Gamma_8^-$ ($E_B = 0.2631$ meV) calculated with $N = 24$ is ~0.6 μeV. *The resolution* is a little *higher* than the best

TABLE I. Convergence of $n\Gamma_8^+$ and $n\Gamma_7^-$ EL's, $n = 1$–10. Binding energies are in units of Ry*. The EL's are computed with radial ODE set orders $N = 4$, 10, 19, and 30 for Γ_8^+; and 3, 7, and 12 for Γ_7^-.

N \ n	30	19	10	4	12	7	3
	Γ_8^+				Γ_7^-		
1	2.3744	2.3736	2.3531	2.3018	0.4924	0.4864	0.4754
2	0.7209	0.7201	0.7083	0.6849	0.2651	0.2601	0.2468
3	0.4951	0.4918	0.4839		0.2350	0.2290	
4	0.3756	0.3750	0.3672	0.3517	0.1722	0.1679	0.1578
5	0.2911	0.2878	0.2818	0.2617	0.1520	0.1469	0.1213
6	0.2792	0.2762	0.2695		0.1220	0.1180	0.1100
7	0.2323	0.2317	0.2254	0.2147	0.1158		
8	0.1884	0.1861	0.1817		0.1069	0.1027	0.0817
9	0.1776	0.1752	0.1684	0.1472	0.0915	0.0877	0.0773
10	0.1701	0.1680	0.1526	0.1452	0.0864		

achieved PTIS line position measurement accuracy in zero external fields [1 μeV for the D line of Al in Ge (Ref. 6)].

In the effective-mass approximation, electric dipole transitions to the odd-parity excited states (ES's) predominantly contribute to PTIS lines, because an absorption of phonon(s) at the second stage of the process diminishes the total transition probability to the valence band. In the case of FIRAS lines at the one-photon absorption process, the transitions to the even-parity states are possible due to the influence of the s-character envelope WF central-cell correction to EMT.[26] We do not consider that Γ_6^+ and Γ_7^+ play an essential role in the transitions, since they have even parity and no s component in their envelope WF decompositions.

An adjustment of the calculated energy spectrum to experimental data was made with help of the B lines for all experimentally studied acceptors (Refs. 5, 6, and 7) except X in Ref. 7 and the C line for X in this reference. The B lines were used instead of D lines[5,6] due to the expectation that the $4\Gamma_8^-$ and $3\Gamma_8^-$ states as the final states of the B and C lines, respectively, are less influenced by a chemical shift than the lower-lying $2\Gamma_8^-$, the final state of the D line.[27]

Let $E_L(B)$ $[E_L(C)]$ be the B (C) line energies, ΔE_L the measurement errors. Then the chemical shift (CS) of the $1\Gamma_8^+$ state and the energy of the ground state (GS) are given by $E_{\mathrm{CS}}(1\Gamma_8^+)=E_L(B)+E_B(4\Gamma_8^-)-E_B(1\Gamma_8^+)$ and $E_{\mathrm{GS}}=E_B(1\Gamma_8^+)+E_{\mathrm{CS}}(1\Gamma_8^+)$, respectively. A positive and negative basis-set truncation and adjustment spectra errors of the CS of $1\Gamma_8^+$ and GS energy are defined as

TABLE II. Binding energies E_B of shallow acceptor in Ge of symmetry $\Gamma_i^{\pm}$, $i=6$, 7, and 8, obtained in this work and as calculated in the spherical model (Ref. 9). The units of energy are meV. a represents the eigenvalues from ODE sets of highest order (first row of coupled E_B values for each EL) and next to highest order (second rows of the couples); an absence of values in the second row means that these EL's were not calculated in the next-to-highest-order N approximation; b represents E_B calculated in the spherical model without and with taking into account the coupling of $nP_{3/2}(\Gamma_8^-)$, $nP_{5/2}(\Gamma_8^-)$ states (first and second rows of E_B couples for Γ_8^- states).

n	Γ_6^+		Γ_7^+		Γ_8^+		Γ_6^-		Γ_7^-		Γ_8^-	
	a	b	a	b	a	b	a	b	a	b	a	b
1	0.8321	1.10	1.1212	1.59	10.3407	9.76	0.7659	0.99	2.1443	2.05	4.5503	4.22
	0.8190		1.1033		10.3369		0.7529		2.1181		4.5312	4.35
2	0.7018	0.685	1.0044	1.28	3.1395	2.90	0.7411	0.73	1.1546	1.08	2.8673	2.75
	0.6896		0.9976		3.1362		0.7244		1.1325		2.8335	2.69
3	0.5768	0.655	0.7134	0.91	2.1563	2.01	0.6142	0.64	1.0232	1.06	2.0912	1.91
	0.5660		0.6979		2.1419		0.6121		0.9972		2.0765	1.97
4	0.5147		0.6590	0.79	1.6358	1.49	0.5269	0.62	0.7499	0.70	1.4786	1.40
	0.5037		0.6521		1.6330		0.5160		0.7310		1.4530	1.35
5	0.4912		0.5191	0.58	1.2677	1.20	0.5184		0.6622	0.675	1.2126	1.09
	0.4808		0.4896		1.2536		0.4981		0.6399		1.2009	1.12
6	0.4258		0.5007		1.2159	1.15	0.4928		0.5314		1.1080	1.03
	0.4167		0.4880		1.2029				0.5140		1.0942	
7	0.3813		0.4689		1.0118	0.90	0.3940		0.5045		0.9304	0.86
	0.3715		0.4609		1.0089		0.3847				0.9111	0.83
8	0.3628		0.3865		0.8205	0.74	0.3856		0.4657		0.7981	0.72
	0.3556				0.8103		0.3655		0.4474		0.7867	
9	0.3284		0.3729		0.7733	0.735	0.3724		0.3984		0.7705	0.69
	0.3205		0.3617		0.7629				0.3820		0.7345	0.71
10	0.2964		0.3653		0.7410	0.67	0.3620		0.3765		0.7302	0.665
	0.2878		0.3592		0.7318						0.7226	
11	0.2878		0.3527		0.6923	0.575	0.3052		0.3525		0.7005	0.57
			0.3422		0.6895		0.2974		0.3313		0.6879	0.55
12	0.2805		0.3379		0.6679		0.2984		0.3466		0.6428	
	0.2755				0.6601		0.2812				0.6277	
13	0.2703		0.2977		0.5781		0.2846		0.3358		0.5667	
	0.2684		0.2790		0.5698		0.2720				0.5563	
14	0.2614		0.2895		0.5441		0.2784		0.3104		0.5396	
	0.2544		0.2774		0.5353				0.2954		0.5076	
15	0.2588		0.2825		0.5230		0.2726		0.2907		0.5144	
					0.5156						0.5025	
16	0.2283		0.2759		0.5145		0.2427		0.2701		0.4830	
	0.2256		0.2630		0.5005		0.2357		0.2560		0.4738	
17	0.2223		0.2599		0.5026		0.2380		0.2667		0.4700	
	0.2182				0.4922		0.2300				0.4580	
18	0.2132		0.2553		0.4817		0.2253		0.2552		0.4645	
	0.2071				0.4695		0.2224		0.2440			

$$\begin{aligned}
\Delta E^{+}_{\mathrm{CS}}(1\Gamma_8^+) &= \{[\Delta E_B(4\Gamma_8^-)-\Delta E_B(1\Gamma_8^+)]^2+[\Delta E_L(B)]^2\}^{1/2}\,, \\
\Delta E^{-}_{\mathrm{CS}}(1\Gamma_8^+) &= -|\Delta E_L(B)|\,, \\
\Delta E^{+}_{\mathrm{GS}} &= \{[\Delta E^{+}_{\mathrm{CS}}(1\Gamma_8^+)]^2+[\Delta E_B(1\Gamma_8^+)]^2\}^{1/2}\,, \\
\Delta E^{-}_{\mathrm{GS}} &= -|\Delta E_L(B)|
\end{aligned} \tag{9}$$

TABLE III. Identification of FIRAS and PTIS data for boron in germanium appropriate to transitions from the ground state. The units of energy are meV.

No. of transition	Final state of transition	Transition energy	Transition energy error	Line label	Line component label	Line position	Line position error
1	$1\Gamma_8^-$	6.248	+0.027	G[a]		6.125[b]	±0.010
2	$2\Gamma_8^+$	7.659	+0.022	E[a]		7.57[c]	±0.01
3	$2\Gamma_8^-$	7.931	+0.038	D[d]		7.936[b]	±0.005
4	$3\Gamma_8^+$	8.642	+0.025	C	C_1[a]	8.686[b]	±0.005
5	$1\Gamma_7^-$	8.654	+0.032		C_2[d]		
6	$3\Gamma_8^-$	8.707	+0.025		C_3[a]		
7	$4\Gamma_8^+$	9.163	+0.022	a[a]		9.06[c]	±0.04
8	$4\Gamma_8^-$	9.320	+0.031	B[e]		9.320[b]	±0.005
9	$5\Gamma_8^+$	9.531	+0.025	b[f]			
10	$6\Gamma_8^+$	9.583	+0.024	$A4$	$A4_1$[a]	9.568[b]	±0.010
11	$5\Gamma_8^-$	9.586	+0.024		$A4_2$[a]		
12	$2\Gamma_7^-$	9.644	+0.029	$A3$	$A3_1$[d]	9.655[b]	±0.010
13	$6\Gamma_8^-$	9.690	+0.025		$A3_2$[a]		
14	$3\Gamma_7^-$	9.775	+0.032	$A2$	$A2_1$[d]	9.785[b]	±0.010
15	$7\Gamma_8^+$	9.787	+0.022		$A2_2$[d]		
16	$7\Gamma_8^-$	9.868	+0.027	$A1$[d]		9.863[b]	±0.010
17	$8\Gamma_8^+$	9.978	+0.023	$I10$	$I10_1$[d]	9.989[b]	±0.010
18	$8\Gamma_8^-$	10.000	+0.024		$I10_2$[a]		
19	$9\Gamma_8^+$	10.025	+0.023	$I9$	$I9_1$[d]	10.048[b]	±0.010
20	$9\Gamma_8^-$	10.028	+0.039		$I9_2$[d]		
21	$1\Gamma_6^-$	10.033	+0.024		$I9_3$[d]		
22	$4\Gamma_7^-$	10.049	+0.027		$I9_4$[d]		
23	$2\Gamma_6^-$	10.058	+0.026		$I9_5$[d]		
24	$10\Gamma_8^+$	10.058	+0.023		$I9_6$[d]		
25	$10\Gamma_8^-$	10.068	+0.023		$I9_7$[a]		
26	$11\Gamma_8^-$	10.098	+0.024	$I8$[f]	$I8_1$		
27	$11\Gamma_8^+$	10.106	+0.022		$I8_2$		
28	$12\Gamma_8^+$	10.131	+0.023	$I7$	$I7_1$[d]	10.139[b]	±0.010
29	$5\Gamma_7^-$	10.136	+0.029		$I7_2$[d]		
30	$12\Gamma_8^-$	10.156	+0.025	$I6$	$I6_1$[a]	10.198[b]	±0.010
31	$3\Gamma_6^-$	10.184	+0.022		$I6_2$[d]		
32	$13\Gamma_8^+$	10.220	+0.023		$I6_3$[a]		
33	$13\Gamma_8^-$	10.232	+0.023	$I5$[f]	$I5_1$		
34	$14\Gamma_8^+$	10.254	+0.023		$I5_2$		
35	$14\Gamma_8^-$	10.259	+0.036		$I5_3$		
36	$6\Gamma_7^-$	10.267	+0.026		$I5_4$		
37	$4\Gamma_6^-$	10.272	+0.024		$I5_5$		
38	$15\Gamma_8^+$	10.276	+0.023		$I5_6$		
39	$5\Gamma_6^-$	10.280	+0.028		$I5_7$		
40	$16\Gamma_8^+$	10.284	+0.025		$I5_8$		
41	$15\Gamma_8^-$	10.284	+0.024		$I5_9$		
42	$7\Gamma_7^-$	10.294	+0.026		$I5_{10}$		

[a] The transition does not satisfy the identification conditions and the final state is considered to be chemically shifted.

[b] Reference 6.

[c] Reference 5.

[d] The transition satisfies the identification conditions.

[e] This line is used for adjustment of the calculated spectrum to the experimental one.

[f] There are no experimental data.

for all SA's except X (Ref. 7), with B replaced by C, and $4\Gamma_8^-$ by $3\Gamma_8^-$ for X in this reference. $\Delta E_B(1\Gamma_8^+)$, $\Delta E_B(n_k\Gamma_k^\pm)$ are the differences (in these calculations always positive) between binding energies calculated with highest and next-to-highest orders N of ODE matrices. The different definitions in (9) are due to the condition $\Delta E_B(4\Gamma_8^-)-\Delta E_B(1\Gamma_8^+)\gg|\Delta E_L(B)|$.

The errors of the CS corrected transition energies $E_T(n_k\Gamma_k^\pm)=E_B(1\Gamma_8^+)-E_B(n_k\Gamma_k^\pm)+E_{\rm CS}(1\Gamma_8^+)$- from the GS to $n_k\Gamma_k^\pm$ states using $\Delta E_{\rm CS}^+(1\Gamma_8^+) >|\Delta E_B(1\Gamma_8^+)-\Delta E_B(n_k\Gamma_k^\pm)|$ read

$$\begin{aligned}\Delta E_T^+(n_k\Gamma_k^\pm)&=\{[\Delta E_B(1\Gamma_8^+)-\Delta E_B(n_k\Gamma_k^\pm)]^2\\&\qquad+[\Delta E_{\rm CS}(1\Gamma_8^+)]^2\}^{1/2}\ ,\\ \Delta E_T^-(n_k\Gamma_k^\pm)&=-|\Delta E_L(B)|\ .\end{aligned}\tag{10}$$

The identification conditions, for example, of the K line by the transition $1\Gamma_8^+\rightarrow n_k\Gamma_k^\pm$ are the following:

$$\begin{aligned}E_T(n_k\Gamma_k^\pm)+\Delta E_T^-(n_k\Gamma_k^\pm)&\le E_L(K)+\Delta E_L^+(K)\ ,\\ E_T(n_k\Gamma_k^\pm)+\Delta E_T^+(n_k\Gamma_k^\pm)&\ge E_L(K)+\Delta E_L^-(K)\ .\end{aligned}\tag{11}$$

If a transition energy $E_T(n_p\Gamma_p^\pm)$ is unsuitable for any close P line position in Eqs. (11), a shift of state $n_p\Gamma_p^\pm$ is defined with its errors as $E_{\rm CS}(n_p\Gamma_p^\pm) =E_T(n_p\Gamma_p^\pm)-E_L(P)$, $\Delta E_{\rm CS}^+(n_p\Gamma_p^\pm)=\Delta E_T^+(n_p\Gamma_p^\pm)$, and $\Delta E_{\rm CS}^-(n_p\Gamma_p^\pm)=-|\Delta E_L(P)|$ (we used that $\Delta E_{\rm CS}^+(1\Gamma_8^+)>|\Delta E_B(1\Gamma_8^+)-\Delta E_B(n_p\Gamma_p^\pm)|$ and $\Delta E_T^+(n_p\Gamma_p^\pm)>|\Delta E_L(P)|$).

Table III gives the identification of FIRAS and PTIS data for B in Ge (Refs. 5 and 6). Similar identifications may be obtained for five other acceptors: Al, Ga, In (Refs. 5, 6, and 7), Be (Ref. 6); and T1 (Ref. 5). In Table IV, we have included the GS CS's and, from the identifications, induced spectroscopic values of the GS binding energies for the nine studied acceptors.

The observed lines corresponding to the transitions from the ground state: G, E, D, C, a, B, $A4$, $A3$, $A2$, $A1$, $I10$, $I9$, $I8$, $I7$, $I6$, and $I5$ were interpreted and a b line is predicted. A number of conclusions may be drawn from the identification. (i) Previously suggested identification of the low-energy lines G, E, D, a, B, C_1, C_2, C_3, and $A1$ (Refs. 28 and 8–13) are confirmed here. There are additions and corrections to the interpretation of other low-energy lines: $A4$, $A3$, $A2$, $I10$, and $I9$ in Refs. 28, 10, and 13. It applies to the $6\Gamma_8^+$, $7\Gamma_8^+$, and $8\Gamma_8^+$ contributions to the $A4$, $A2$, and $I10$ lines, respectively, the absence of the $1\Gamma_6^-$ as the final state of the $A3$ line, and the distribution of the $8\Gamma_8^-$, $2\Gamma_6^-$, and $9\Gamma_8^-$ among the final states of the $I10$ and $I9$ lines in this work (cf. Ref. 13). (ii) From 17 analyzed lines, ten lines have multiplet structure (not taking into account degeneracy in the cubic symmetry): $A4$, $A3$, $A2$, $I10$, $I8$, and $I7$

TABLE IV. Ground-state chemical shifts $E_{\rm CS}$, CS calculation errors $\Delta E_{\rm CS}^\pm$, spectroscopic ground-state binding energies $E_{\rm GS}$, and GS calculation errors $\Delta E_{\rm GS}^\pm$ of the experimentally studied acceptors. The units of energy are meV.

	Acceptor								
	B	Al	Ga	In	X[a]	Y	Be	X[b]	T1
				Present calculations					
$E_{\rm CS}$	0.458[c]	0.792[c]	0.952[c]	1.644[c]	0.644[c]	1.908[c]	14.468[c]	1.285[d]	3.058[e]
$\Delta E_{\rm CS}^+$	+0.022	+0.022	+0.022	+0.024	+0.024	+0.024	+0.030	+0.011	+0.024
$\Delta E_{\rm CS}^-$	−0.005	−0.002	−0.005	−0.010	−0.010	−0.01	−0.02	−0.002	−0.01
$E_{\rm CS}$		0.802[f]	0.962[f]						
$\Delta E_{\rm CS}^+$		+0.022	+0.022						
$\Delta E_{\rm CS}^-$		−0.002	−0.002						
$E_{\rm GS}$	10.799	11.133	11.293	11.985	10.985	12.249	24.809	11.626	13.399
$\Delta E_{\rm GS}^+$	+0.023	+0.022	+0.023	+0.024	+0.024	+0.024	+0.030	+0.012	+0.024
$\Delta E_{\rm GS}^-$	−0.005	−0.002	−0.005	−0.010	−0.010	−0.01	−0.02	−0.002	−0.01
$E_{\rm GS}$		11.143	11.303						
$\Delta E_{\rm GS}^+$		+0.022	+0.022						
$\Delta E_{\rm GS}^-$		−0.002	−0.002						
				Reported data					
$E_{\rm GS}$	10.57[g]	10.90[g]	11.07[g]	11.74[g]	10.74[g]	12.01[g]	24.54[g]		
$\Delta E_{\rm GS}^\pm$	±0.01	±0.01	±0.01	±0.01	±0.01	±0.01	±0.03		
$E_{\rm GS}$	10.47[h]	10.80[h]	10.97[h]	11.61[h]					13.10[h]

[a] Acceptor from Ref. 6.

[b] Acceptor from Ref. 7.

[c] Spectra adjustment with help of B line from Ref. 6.

[d] Spectra adjustment with help of C line from Ref. 7.

[e] Spectra adjustment with help of B line from Ref. 5.

[f] Spectra adjustment with help of B line from Ref. 7.

[g] Reference 6.

[h] Reference 5.

doublet; *C*-, *I*6 triplet, *I*9 septet, and *I*5 decuplet. (iii) Many of the acceptor line components, essentially of high energy, overlap one another. Therefore the precise characterization of the impurity presence in the material will demand a calculation of many of the line positions and their oscillator strengths to account for the complicated picture of the different acceptor line overlapping. (iv) Inspection of Table III indicates that a number of lines (including singlets) were not identified when tested by conditions (11). Their final states are supposed to be chemically shifted.[29] The CS's of the even-parity ES's, e.g., $2\Gamma_8^+$ (the final state of the *E* line) are well known. On the other hand, these effects have been observed in SA spectra associated with transitions between both even- and odd-parity ES's. For instance, the observations of 61 (Ref. 8) and 82 (Ref. 9) PTIS lines for Ge(B). The 44th and 45th lines in Ref. 8 were interpreted as transitions $1\Gamma_8^- \rightarrow 1\Gamma_7^-$ and $1\Gamma_8^- \rightarrow 3\Gamma_8^-$. The positions of these lines show the

TABLE V. Excited-state chemical shifts $E_{\rm CS}$ and CS calculation errors $\Delta E_{\rm CS}^{\pm}$ deduced from the spectroscopic data on the experimentally studied acceptors. The units of energy are meV.

	B									
	$1\Gamma_8^-$	$2\Gamma_8^+$	$3\Gamma_8^+$	$3\Gamma_8^-$	$4\Gamma_8^+$	$6\Gamma_8^+$	$5\Gamma_8^-$	$6\Gamma_8^-$	$8\Gamma_8^-$	$10\Gamma_8^-$
$E_{\rm CS}$	$0.033^{\rm a}$	$0.089^{\rm b}$	$-0.044^{\rm a}$	$0.021^{\rm a}$	$0.103^{\rm b}$	$0.014^{\rm a}$	$0.018^{\rm a}$	$0.036^{\rm a}$	$0.011^{\rm a}$	$0.020^{\rm a}$
$\Delta E_{\rm CS}^{+}$	+0.027	+0.022	+0.025	+0.025	+0.022	+0.024	+0.024	+0.025	+0.024	+0.023
$\Delta E_{\rm CS}^{-}$	−0.010	−0.01	−0.005	−0.005	−0.04	−0.010	−0.010	−0.010	−0.010	−0.010

	Al										
	$1\Gamma_8^-$	$2\Gamma_8^+$	$3\Gamma_8^+$	$1\Gamma_7^-$	$3\Gamma_8^-$	$6\Gamma_8^-$	$7\Gamma_8^-$	$8\Gamma_8^-$	$2\Gamma_6^-$	$10\Gamma_8^+$	$10\Gamma_8^-$
$E_{\rm CS}$	$0.017^{\rm a}$	$0.059^{\rm c}$	$-0.049^{\rm a}$	$-0.037^{\rm a}$	$0.016^{\rm a}$	$0.030^{\rm a}$	$0.004^{\rm a}$	$0.014^{\rm a}$	$0.010^{\rm a}$	$0.010^{\rm a}$	$0.020^{\rm a}$
$\Delta E_{\rm CS}^{+}$	+0.027	+0.022	+0.024	+0.031	+0.025	+0.024	+0.027	+0.023	+0.026	+0.023	+0.022
$\Delta E_{\rm CS}^{-}$	−0.005	−0.002	−0.002	−0.002	−0.002	−0.002	−0.002	−0.01	−0.002	−0.002	−0.002
$E_{\rm CS}$	$0.012^{\rm c}$		$-0.044^{\rm c}$		$0.021^{\rm c}$	$0.034^{\rm c}$	$0.004^{\rm c}$	$0.004^{\rm c}$	$0.007^{\rm c}$	$0.007^{\rm c}$	$0.018^{\rm c}$
$\Delta E_{\rm CS}^{+}$	+0.027		+0.024		+0.025	+0.024	+0.027	+0.023	+0.026	+0.023	+0.022
$\Delta E_{\rm CS}^{-}$	−0.002		−0.002		−0.002	−0.002	−0.002	−0.002	−0.002	−0.002	−0.002

	Ga							
	$1\Gamma_8^-$	$2\Gamma_8^+$	$3\Gamma_8^+$	$3\Gamma_8^-$	$6\Gamma_8^-$	$2\Gamma_6^-$	$10\Gamma_8^+$	$10\Gamma_8^-$
$E_{\rm CS}$	$0.022^{\rm a}$	$0.133^{\rm b}$	$-0.049^{\rm a}$	$0.016^{\rm a}$	$0.032^{\rm a}$	$0.016^{\rm a}$	$0.016^{\rm a}$	$0.026^{\rm a}$
$\Delta E_{\rm CS}^{+}$	+0.027	+0.022	+0.025	+0.025	+0.025	+0.026	+0.023	+0.023
$\Delta E_{\rm CS}^{-}$	−0.005	−0.02	−0.005	−0.005	−0.010	−0.010	−0.010	−0.010
$E_{\rm CS}$			$-0.045^{\rm c}$	$-0.020^{\rm c}$				
$\Delta E_{\rm CS}^{+}$			+0.024	+0.025				
$\Delta E_{\rm CS}^{-}$			−0.002	−0.002				

	In									
	$1\Gamma_8^-$	$2\Gamma_8^+$	$3\Gamma_8^+$	$3\Gamma_8^-$	$4\Gamma_8^+$	$6\Gamma_8^+$	$5\Gamma_8^-$	$6\Gamma_8^-$	$7\Gamma_8^+$	$7\Gamma_8^-$
$E_{\rm CS}$	$0.044^{\rm b}$	$0.425^{\rm b}$	$-0.036^{\rm a}$	$0.029^{\rm a}$	$0.149^{\rm b}$	$0.023^{\rm a}$	$0.026^{\rm a}$	$0.048^{\rm a}$	$0.018^{\rm a}$	$0.021^{\rm a}$
$\Delta E_{\rm CS}^{+}$	+0.028	+0.024	+0.026	+0.026	+0.024	+0.026	+0.025	+0.026	+0.024	+0.029
$\Delta E_{\rm CS}^{-}$	−0.01	−0.01	−0.005	−0.005	−0.03	−0.015	−0.015	−0.010	−0.010	−0.010

	$X^{\rm d}$		Y		
	$3\Gamma_8^+$	$3\Gamma_8^-$	$3\Gamma_8^+$	$3\Gamma_8^-$	$6\Gamma_8^-$
$E_{\rm CS}$	$-0.042^{\rm a}$	$0.023^{\rm a}$	$-0.038^{\rm a}$	$0.027^{\rm a}$	$0.020^{\rm a}$
$\Delta E_{\rm CS}^{+}$	+0.026	+0.026	+0.026	+0.026	+0.026
$\Delta E_{\rm CS}^{-}$	−0.010	−0.010	−0.01	−0.01	−0.01

	Be					Tl				
	$2\Gamma_8^-$	$3\Gamma_8^+$	$1\Gamma_7^-$	$3\Gamma_8^-$	$2\Gamma_7^-$	$2\Gamma_8^+$	$3\Gamma_8^+$	$1\Gamma_7^-$	$4\Gamma_8^+$	$6\Gamma_8^-$
$E_{\rm CS}$	$0.031^{\rm a}$	$-0.208^{\rm a}$	$-0.096^{\rm a}$	$-0.143^{\rm a}$	$-0.076^{\rm a}$	$0.429^{\rm b}$	$-0.078^{\rm b}$	$-0.066^{\rm b}$	$0.113^{\rm b}$	$0.030^{\rm b}$
$\Delta E_{\rm CS}^{+}$	+0.042	+0.032	+0.037	+0.032	+0.035	+0.024	+0.026	+0.033	+0.024	+0.026
$\Delta E_{\rm CS}^{-}$	−0.02	−0.02	−0.02	−0.02	−0.02	−0.04	−0.02	−0.02	−0.02	−0.03

[a] Line position from Ref. 6.
[b] Line position from Ref. 5.
[c] Line position from Ref. 7.
[d] Acceptor from Ref. 6.

dependence on the chemical nature of the impurity which have led the authors of Ref. 9 to conclude that there is the $1\Gamma_8^-$ state CS. Here the ES CS's are deduced from identification of GS-ES's transitions. Table V summarizes the CS's derived in that way for the first 25 ES's. Although the values of some of these shifts are less than the linewidths or instrumental resolution and the negative CS's appear to be (the measured line peak in some cases are inadequate to the calculated transition energies), a trend of the excited-state chemical shifts may be perceived.

An observation of the spectral line fine structure and the measurement of the energy splitting of the multiplets is crucial to confirming the identification. As may be seen from Tables II and III, the splittings of $3\Gamma_8^+ - 1\Gamma_7^-$ and $1\Gamma_7^- - 3\Gamma_8^-$ inside the C triplet are estimated as 12 and 53 μeV, respectively. The first value is within the reported instrumental resolution of 30 μeV (Ref. 6). The second is in agreement with the PTIS measurement of the $C'^* - C^*$ splittings of ~ 50 μeV both for Ge(B) and Ge(Al) and is close to the ~ 40-μeV splitting for Ge(In) (Ref. 8). The value is consistent with the estimation of this ~ 40-μeV splitting deduced from the FIRAS data on Ge(Zn^-).[30] It should be emphasized that the energy splittings in multiplets do not depend on the chemical nature of the acceptor. One should note that random electric fields caused by charged impurities as well as random strains may influence linewidth[7] and conceal the splittings.

A comparison of the data in Tables II and IV shows that the calculated valence-band warping lowering of the $1\Gamma_8^+$ EL and the GS CS, for example, for Ge(B), are ~ 580 and ~ 460 μeV, respectively. In the spherical model the sum of these values was used for adjustment of the calculated $E_B(1\Gamma_8^+)$ to the experimentally observed GS binding energy by means involving q dependent screening and short-range potential instead of using the value of 460 μeV of the CS which is actually responsible for these contributions. This implies an overestimation of the short-range potential as well as the q-dependent screening considered in previous work.[10–13]

IV. CONCLUSION

We have shown that a method of singular boundary problem numerical analysis of radial ODE sets may be used for a controlled-accuracy solution of the EMT equation. The method presented here also can be used to perform computations and evaluate the high ES-dependent properties of shallow impurities in bulk material and heterostructures. For instance, this technique is an ideal tool to study the excitons in bulk and quantum wells. The calculations are intended to be definitive, and a systematic attempt has been made to interpret PTIS and FIRAS data on SA's in Ge. The calculated transition energies are in good agreement with corresponding experimental data. To comment briefly on some of the computed results, we should note that in the spectral region studied more than 100 EL's exist which give rise to a few hundred transitions for different SA's. The stable trend of the odd-parity ES CS's raises the question about the origin of the shifts. It also indicates limitations of the central cell corrections requiring more work in chemical effects from first principles. We should not close without emphasizing the highly satisfactory situation of application of the singular boundary problem numerical analysis to a study of centers in ultrapure materials. The reason is that the method is based on the analytically proved existence, uniqueness, representation, and stability of the numerical solution of ODE. In that way we obtain a controlled-accuracy, well-convergent solution of the EMT equation for the acceptor problem.

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[26] This is supported by the absence of transition $1\Gamma_8^+ \rightarrow 2\Gamma_8^+$ leading to E lines in PTIS spectra (Ref. 6), while the lines are observed in FIRAS spectra (Ref. 5).

[27] If the chemical shifts of the $4\Gamma_8^-$ states exist they should be added to the data on the transition energies of Table III, the GS binding energies and CS's of Table IV, and the ES CS's of Table V.

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