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Response to "Comment on 'A comparative study of *ab initio* nonradiative recombination rate calculations under different formalisms"

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We address two issues in this response. One is the error pointed out by Wickramaratne *et al.* in their comment Ref.[1], another is a mix-up for the configurations used to expand the Hamiltonian. In Ref.[1], the authors pointed out a possible error in our calculation of the "one-dimensional (1D) quantum formula" in our paper Ref.[2]. We thank them for their comment, and indeed we do find an algebra error in our original calculations. This response thus should serve as an erratum of Ref.[2]. We also like to take this opportunity to clarify another issue in Ref.[2] which presented confusingly in the original paper. This issue is for which atomic configuration to be used as the origin of expansion for the Hamiltonian H: the initial Q_i configuration or the final Q_j configuration. By correcting these issues, new insights have been obtained when comparing the quantum mechanical static coupling formalism with the effective 1D formalisms.

After we went through the original calculations in Ref.[2], we found that we made a mistake in the calculation of $\hbar\Omega_j$ (missing a factor of $\sqrt{2}$) in the case of GaP:Zn_{Ga}-O_P. As a result, the original Fig.7 is wrong, and the calculated value of Q_c is incorrect. The correct Q_c value in our calculation should be 5.50 amu^{1/2}Å, instead of 19.09 amu^{1/2}Å. We now provide a corrected replacement (Fig.1 here) of the original Fig.7.

For the second issue, we are calculating the process of electron jumping into the defect state from the conduction band state (the energy is going down, from red curve to black curve in Fig.7). So, the initial state is "i" and final state is "i" in our notation and in the following discussions. There was a mix-up in comparing the 3D static result and all the other effective 1D formalisms (Marcus, Quantum Charge Transfer (QCT), and 1D model in the work of Alkauskas, Yan and Van de Walle (AYV-1D) [3]). For the 3D static result in Ref.[2], the expansion for Hamiltonian H is done at Q_i , while for all the effective 1D formalisms, the expansion was done at Q_j (our Eq.(30) of Ref.[2] should be $V_c = \langle \psi_i(Q_i) | H(Q_c) | \psi_i(Q_i) \rangle = \langle \psi_i | \partial H / \partial Q | \psi_i \rangle \langle Q_c - Q_i \rangle$. In Eq.(30) of Ref.[2], we had used $Q_c - Q_i$ instead of $Q_c - Q_j$.). Actually, there is no prior reason for the expansion to be done at Q_i or Q_j . Here, for better comparisons, we will show the results for expansion at Q_i and Q_j separately for all the formalisms. Note, in order to calculate the 3D static formalism with the expansion at point Q_j , one only needs to change Eq.(26a) of Ref.[2] to $D_{HT} = D^{-1}d(\tau_i)\mathbf{K}$, Eq.(27) and all the rest of the formalism are the same. In the following calculations, we have used the coupling constants C_{ij}^k of Eq.(18) in Ref.[2] calculated at Q_i in both Q_i and Q_j expansion formalisms. We believe these coupling constants do not change significantly, and this is a general underlying approximation of Harmonic expansions in deriving all of the above formalisms. After this rearrangement, and the correction of our previous mistakes of the factor of $\sqrt{2}$ error in the case of GaP:Zn_{Ga}-O_p, we now have the new curves shown in Fig.2 for the case of GaP:Zn_{Ga}-O_P with H expansions at Q_j (Fig.2(a)) and Q_i (Fig.2(b)) respectively. The same calculations are done in the case of $GaN:Zn_{Ga}-V_N$, and the results are plotted in Fig.3. The capture coefficient B_p is obtained by dividing the capture cross section by the electron thermal velocity. In order to compare the results of GaP:Zn_{Ga}-O_P and GaN:Zn_{Ga}-V_N , we have used the capture coefficient for both cases. Now, the situations for GaP: Zn_{Ga} -O_P and the GaN: Zn_{Ga} -V_N become very similar. Compared with the original Fig.8 in Ref.[2], in our current Fig.2(a), the curve of AYV-1D is significantly changed and the curves of Marcus and QCT have also been shifted down. Similarly, compared with the original Fig.10 in Ref.[2], in our current Fig.3(a), the curve of AYV-1D is corrected and the Marcus and QCT curves are unchanged. To make the calculation clear, we have listed the parameters used in calculating all these curves in Table.I for both GaP:Zn_{Ga}-O_P and GaN:Zn_{Ga}-V_N cases. We note that our parameters for GaP:Zn_{Ga}-O_P are now very close to the parameters listed in the comment by Wickramaratne *et al* Ref.[1]. The AYV-1D (referred to as 1D in the figure legends) is calculated using two different numerical methods. One is to use Eq.(21),(27) of Ref.[2] but making all the matrix one dimensional. Another is to use the direct summation based on Eq.(19) using the computer code gracefully provided by A. Alkauskas. These two numerical approaches yield almost the same results, which can serve as a test to the formalism of Eq.(21), (27) of Ref.[2]. We also note that, the Fig.9 in Ref.[2] represent the dependence of the capture coefficients as function of defect energy. For that figure, after the above corrections, the "1D quantum formula" curve will become close to the Marcus and quantum CT curves, and all three of them will shift down, while the static and adiabatic curves will not change, as shown in Fig.4.



FIG. 1. (Color online) Calculated 1D cc diagram for Zn_{Ga}-O_P center in GaP.



Fig. 2. (Color online) Capture coefficient for the Zn_{Ga} -O_P center in GaP. (a) all the formalisms with the H expansion point at Q_j ; (b) all the formalisms with H expansion point at and Q_i ; and (c) comparison of the 3D static theory results at different expansion points. The stars are experimental data from Ref. [4], the experimental capture coefficient is obtained by dividing the experimental capture cross section by the electron thermal velocity.







Fig. 3. (Color online) Capture coefficient for the $Zn_{Ga}-V_N$ center in GaN. (a) all the formalisms with the H expansion point at Q_j ; (b) all the formalisms with H expansion point at and Q_i ; and (c) comparison of the 3D static theory results at different expansion points. The star is experimental data from Ref. [5].



Fig.4. (Color online) Capture coefficients as function of ΔE for Zn_{Ga} -O_P center in GaP when T=300 K.

		$\left Q_{i} - Q_{j} \right $	$\hbar\Omega_{j}$	\mathbf{S}_{j}	W _{ij}	ΔE_{ij}	λ	$Q_C - Q_j$	V_{C}
		(amu ^{1/2} Å)	(meV)		(eV/amu ^{1/2} Å)	(eV)	(eV)	(amu ^{1/2} Å)	(eV)
GaP:Zn _{Ga} -O _P	In this work	4.43	8.99	21.12	0.25×10 ⁻²	0.282	0.19	5.50	0.014
	Ref.[1]	4.68	9.51	24.07	0.31×10 ⁻²	0.253	0.23		
GaN:Zn _{Ga} -V _N	In this work	3.13	23.37	27.39	1.0×10^{-2}	0.91	0.64	3.79	0.038
	Ref.[3]	3.33	22	30	1.0×10 ⁻²	0.88	0.62		

TABLE I. The key variables calculated for the 1D quantum formula method, Marcus theory and quantum CT rate

We now provide some discussions for all these results in order to understand the similarities and differences between different formalisms. First, the AYV-1D result is rather similar to the QCT and Marcus results, this is in qualitative agreement of comments made in Ref.[1]. For the QCT result, although its H expansion is done in 1D, its phonon degree of freedom (the summation over n and m in Eq.(31) of Ref.[2]) is calculated in 3D. The fact that the QCT result is so close to the AYV-1D result, which is calculated with a 1D phonon mode, indicates that this 3D phonon treatment might be similar to the 1D phonon treatment. To test this further, we have used a 1D effective phonon mode as defined in Ref.[4] to carry out the $\sum_{n,m} |\langle \phi_{j,m} | \phi_{i,n} \rangle|^2$ (here $\phi_{j,m}$ and $\phi_{i,n}$ are phonon states at electrons states *j* and *i*, with phonon configuration *m* and *n* respectively) summation in Eq.(31) of Ref.[2] (in actual calculation, replacing the sum over *k* in Eq.(33) of Ref.[2] by one effective phonon mode along the $Q_i - Q_j$ direction). The result will be called QCT-1D to distinguish with the original QCT-3D result (which is shown in Fig.2). Their comparison is provided in Fig.5. The similarity of QCT-3D and QCT-1D shown in Fig.5 indicates that the 3D phonon treatment.

The difference between QCT-1D and AYV-1D is in their treatment of $\sum_{n,m} |\langle \phi_{j,m} | (Q-Q_a) | \phi_{i,n} \rangle|^2$ (here Q_a is Q_i or Q_j). In QCT-1D, the $Q-Q_a$ is approximated by $Q_c - Q_a$, and pulled out from the bracket before the summation over n,m, while

in AYV-1D, the $Q-Q_a$ operator is kept inside the bracket during the n,m summation. The fact that their results are so similar as shown in Fig.2, Fig.3 and Fig.4 means indeed in the phonon summation, it statistically samples mostly the Q_c point, in agreement with the classical limit intuition that Q_c point is the transition barrier point, which critically determines the transition rate, as in the derivation of the Marcus theory.



Fig.5. For the capture coefficients of $GaP:Zn_{Ga}-O_{P,}$ comparison between quantum CT rate 3D and 1D.

Then the issue is, why in our 3D static treatment, we cannot replace $Q - Q_a$ by $Q_c - Q_a$ in Eq.(14) of Ref.[2]. If we do that, our 3D static model will become exactly the same as the QCT-3D model. But as shown in Fig.2 and 3, the static model result is much larger than the QCT-3D result.

Note, in Eq.(14) of Ref.[2], if we place the sum over k inside the bracket, it becomes: $\langle \phi_{j,m} | \sum_{k} C_{ij}^{k} (Q_{k} - Q_{i,k}) | \phi_{i,n} \rangle$, this is almost like a 1D formalism (in terms of $Q - Q_{i}$ expansion of H). However, compared to the 1D H expansion in QCT and AYV-1D, this expansion is along (or say projecting $Q - Q_i$ to) the direction of C_{ij}^k , instead of $Q_j - Q_i$. Note, the direction of $Q_j - Q_i$ is determined by the diagonal electron-phonon coupling constants: $C_{jj}^k - C_{ii}^k$, which can be very different from that of C_{ij}^k , especially in the high dimensional case. Indeed, we have calculated the dot product of C_{ij}^k unit vector (in the 3N dimension of k, here N is the number of atoms) and the $Q_j - Q_i$ unit vector. The dot product is -0.0029 for the GaP:Zn_{Ga}-O_P, thus they are almost orthogonal.

As discussed above, the phonon summation over m,n will sample heavily near the Q_c point, but nevertheless, it can deviate a little bit (in the finite temperature case) from Q_c . While in the 1D formalism like AYV-1D, the deviation is confined in the $Q_j - Q_i$ direction, thus a small deviation will not make any large difference. But in the 3D case, a small deviation in the direction of C_{ij}^k can make a relatively large difference due to the almost perpendicular direction between C_{ij}^k and $Q_j - Q_i$. It is this freedom in the C_{ij}^k direction which provides the majority of the contribution to the transition rate in the 3D static formalism. One can estimate how large this deviation can be and what can be its contribution to $\sum_{k} C_{ij}^{k} (Q - Q_{c})$. If we assume the effective phonon mode along the C_{ij}^k direction has a strength similar to the effective phonon mode in the $Q_i - Q_j$ direction shown in Fig.1, and the deviation can have an energy increase of kT, then the dQ can be in the order of 1 amu^{1/2}Å at room temperature. Such a dQ in the C_{ij}^k direction will have a much larger $\sum_{k} C_{ij}^{k} dQ$ than the $\sum_{k} C_{ij}^{k} (Q_{j} - Q_{i})$ (almost a factor of 100 larger). According to this, the static formula should have even bigger result. The fact its result is smaller than this simple estimation is probably because the deviation energy kT is not solely used in the direction along C_{ij}^k , or the effective phonon mode along the C_{ij}^k direction is much stronger. Nevertheless, this estimation shows the deviation should be strong enough to provide a large contribution to $\sum_{k} C_{ij}^{k} dQ$.

The above analysis also explains, why the 3D static formalism result is insensitive to the choice of using Q_i and Q_j as the expansion point of H, while the results of all the other (effective 1D) formalisms can change by a factor of 10 as shown in Fig.2 and 3. This is because the majority of the contribution in the 3D static formalism comes from the perpendicular direction deviation from the Q_c point in the C_{ij}^k direction, which is independent of whether Q_i or Q_j is used as the H expansion point. Unfortunately, without calculating C_{ij}^k , there is no way to know this gradient direction of the H expansion.

Lastly, we also like to take this opportunity to correct a typo in the original Ref.[2]. The Eq.(15) should be written as: $\mathbf{Q}_{(i,j)k} = \sum_{R} \sqrt{M_R} \mu_k(R) \mathbf{R}_{(i,j)}$, while the orthonormal condition is: $\sum_{R} \mu_k(R) \mu_l(R) = \delta_{k,l}$. We also like to point out, in 1D, if $(A_{HT})_{kk}$ in the Eq.(27) of Ref.[2] is replaced by $(Q_c - Q_i)^2$, then Eq.(27) becomes the same as the Eq.(33) of the QCT-1D formalism.

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