Supplementary Information: Fröhlich polaron effective mass and localization length in cubic materials: degenerate and anisotropic electronic bands

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(I) Supplementary theory
(II) Supplementary figures
(III) Supplementary tables

I. SUPPLEMENTARY THEORY

A. Polaron localization length asymptotic behavior in the uniaxial limit

Based on the electronic effective masses, we provide analytical formulas for the asymptotic behaviour of the localization lengths in the non-degenerate anisotropic case. We determine the spherical average asymptotic behaviour in the low limit of \( \mu^* \) (as defined in the main text), Eq. S1, respectively high limit - Eq. S5. Similarly, we follow with the two meaningful localization lengths \( a_{P_z} \) (Eq. S2 and Eq. S6), respectively \( a_{P_{\perp}} \) (Eq. S3 and Eq. S7), and polaron formation energy (Eq. S4 and Eq. S8).

\[
\lim_{\mu^* \to 0} a_P = 2 \left( \frac{\pi}{2} \right)^{-5/2} m_{\perp}^{-1} e^* \left( \frac{\pi \mu^*}{4} \right)^{1/9} \quad (S1)
\]

\[
\lim_{\mu^* \to 0} a_{P_z} = 2 \left( \frac{\pi}{2} \right)^{-5/2} m_{\perp}^{-1} e^* \left( \frac{\pi \mu^*}{4} \right)^{1/3} \quad (S2)
\]

\[
\lim_{\mu^* \to 0} a_{P_{\perp}} = 2 \left( \frac{\pi}{2} \right)^{-5/2} m_{\perp}^{-1} e^* \quad (S3)
\]

\[
\lim_{\mu^* \to 0} E_P(\mu^*) = -\frac{\pi}{16} m_{\perp}^{-1} (e^*)^{-2} \quad (S4)
\]

\[
\lim_{\mu^* \to \infty} a_P = 4 \sqrt{2 \pi m_{\perp}^{-1} (\mu^*)^2} \left( \frac{3 \epsilon^* (\log(4 \mu^*))^2 (\log(4 \mu^*))^{-2} (\log(4 \mu^2) - 2 - \log(\log(4 \mu^2) - 2))^{-2/3} \right) \quad (S5)
\]

\[
\lim_{\mu^* \to \infty} a_{P_z} = 4 \sqrt{2 \pi m_{\perp}^{-1} \mu e^* (\log(4 \mu^*))^2 (\log(4 \mu^*))^{-2} (\log(4 \mu^2) - 2 - \log(\log(4 \mu^2) - 2))^{-1} \quad (S6)
\]
\[
\lim_{\mu^* \to \infty} a_{P_+} = 4\sqrt{2\pi m^{-1}_z} (\mu^*)^{1/2} \epsilon^* (\log(4\mu^*))^2 (\log(4\mu^*))^{-2} (\log(4\mu^2) - 2 - \log(4\mu^*) - 2)^{-1/2}
\]

(S7)

\[
\lim_{\mu^* \to \infty} E_P(\mu^*) = -\frac{1}{8\pi} m_z (\epsilon^*)^{-2} (\log(4) + \log(\mu^*))^2
\]

(S8)

In our representation inside the main text we are working at a constant density of states, thus we can define the effective mass in the following way, considering that \( m_x = m_y = m_\perp \):

\[
m^*_\text{DoS} = (m_x m_y m_z)^{1/3}
\]

(S9)

\[
m_z = m^*_\text{DoS}(\mu^*)^{-2/3}
\]

(S10)

\[
m_\perp = m^*_\text{DoS}(\mu^*)^{1/3}
\]

(S11)

Consequently, the asymptotic behaviour for the different localization lengths and formation energy are defined as:

\[
\lim_{\mu^* \to 1} a_{P} = \frac{3}{2} \sqrt{2\pi m^1_{\text{DoS}}} \epsilon^* \left(1 + \frac{3}{14} (\mu^* - 1)\right)
\]

(S12)

\[
\lim_{\mu^* \to 1} a_{P_x} = \frac{3}{2} \sqrt{2\pi m^1_{\text{DoS}}} \epsilon^* \left(1 + \frac{2}{21} (\mu^* - 1)\right)
\]

(S13)

\[
\lim_{\mu^* \to 1} a_{P_\perp} = \frac{3}{2} \sqrt{2\pi m^1_{\text{DoS}}} \epsilon^* \left(1 + \frac{19}{42} (\mu^* - 1)\right)
\]

(S14)

\[
\lim_{\mu^* \to 1} E_P(\mu^*) = -\frac{1}{6\pi} m^1_{\text{DoS}} (\epsilon^*)^{-2}
\]

(S15)

**B. Polaron properties in the ellipsoidal limit**

In the case of the tri-axial ellipsoidal limit we provide an approximate solution to the polaron localization length and formation energy. We base our estimation on the formalism provided in the asymptotic non-degenerate case where we have the exact solution for the cases of \( m^*_x = m^*_y \neq m^*_z \) (and their commutative counterparts). Thus we estimate the average localization length in the cases where \( m^*_x \neq m^*_y \neq m^*_z \) considering a cosine interpolation function, as defined in Eq. [S18] while working under the constant volume condition, as defined in Eq. [S16]

\[
a_{P} = (a_{P_x} a_{P_y} a_{P_z})^{1/3}
\]

(S16)

\[
\delta_\sigma = \exp (\sigma \sqrt{6}|\epsilon|) - 1; \sigma = \pm
\]

(S17)

\[
\ln <a> = \ln a_P - \frac{1}{2} \sum_{\sigma = \pm} (1 + \sigma \cos(3\theta))(1 + \delta_\sigma)^{1/6} S(\delta_\sigma)
\]

(S18)
\[ |c| = \left( \frac{2}{3} \left( \ln^2 a_{px} + \ln^2 a_{py} + \ln^2 a_{pz} - \ln a_{px} \ln a_{py} - \ln a_{px} \ln a_{pz} - \ln a_{pz} \ln a_{px} \right) \right)^{1/2} \]  

\[ \frac{\partial \ln <a>}{\partial a_{pz}} = 3a_{pz} + \frac{1}{2} \sum_{\sigma = \pm} \left\{ \frac{\partial}{\partial a_{pz}} \left[ \cos(3\theta) \right] \frac{1}{(1 + \delta_{\sigma})^{1/6} S(\delta_{\sigma})} \right\} \]  

\[ \cos(3\theta) = \frac{4}{(\sqrt{6}|c|)^3} \ln \left( \frac{a_{px} a_{py}}{a_{pz}^2} \right) \ln \left( \frac{a_{pz} a_{px}}{a_{py}^2} \right) \ln \left( \frac{a_{py} a_{pz}}{a_{px}^2} \right) \]  

\[ \frac{\partial}{\partial a_{pz}} \left[ \cos(3\theta) \right] = \cos(3\theta) \left[ -\frac{3}{|c|} \frac{\partial |c|}{\partial a_{pz}} + a_{pz} \left( \ln \left( \frac{a_{px} a_{pz}}{a_{py}^2} \right)^{-1} + \ln \left( \frac{a_{py} a_{pz}}{a_{px}^2} \right)^{-1} - 2 \ln \left( \frac{a_{px} a_{py}}{a_{pz}^2} \right)^{-1} \right) \right] \]  

\[ \frac{\partial |c|}{\partial a_{pz}} = \frac{a_{pz}}{|c|} \ln \left( \frac{a_{pz}^2}{a_{px} a_{py}} \right) \]  

\[ \frac{\partial}{\partial a_{pz}} \left[ (1 + \delta_{\sigma})^{1/6} S(\delta_{\sigma}) \right] = \frac{\partial \delta_{\sigma}}{\partial a_{pz}} \left[ \frac{1}{6} (1 + \delta_{\sigma})^{-5/6} S(\delta_{\sigma}) + (1 + \delta_{\sigma})^{1/6} \frac{dS}{d\delta_{\sigma}} \right] \]  

\[ \frac{\partial \delta_{\sigma}}{\partial a_{pz}} = \sigma \sqrt{6} (\delta_{\sigma} + 1) \frac{\partial |c|}{\partial a_{pz}} \]
II. SUPPLEMENTARY FIGURES

FIG. S1: Average squared effective mass in the uniaxial limit calculated at constant density of states expressed in terms of $\mu^*$. In the low limit of $\mu^*$, the asymptotic analytical behaviour is represented in orange. In the $\mu^* \to 1$ limit, the analytical expression is represented in red. Finally, in the large $\mu^*$ limit, the asymptotic behaviour analytical limit is represented in green. We consider here $\epsilon^* = 1$. 

\[
\begin{align*}
(1/2)\mu^*^{-3/2}\ln(4\mu^*) \\
1 - 1/45(\mu^* - 1) ; \mu^* \to 1 \\
(\pi/2)(\mu^*)^{1/6}
\end{align*}
\]
### III. SUPPLEMENTARY TABLES

**TABLE S1**: *ab initio* DFT convergence parameters for the studied materials such as: kinetic energy cut-off in the plane-wave basis set, electronic states wavevector (k-point) sampling.

| Material | Ecut(Ha) | k-point sampling |
|----------|----------|------------------|
| AlAs     | 40       | 6x6x6 (x4 shifts) |
| AlN      | 35       | 6x6x6           |
| AlP      | 25       | 8x8x8 (x4 shifts) |
| AlSb     | 40       | 6x6x6 (x4 shifts) |
| BAs      | 40       | 6x6x6 (x4 shifts) |
| BN       | 35       | 8x8x8           |
| CdS      | 45       | 6x6x6 (x4 shifts) |
| CdSe     | 50       | 6x6x6 (x4 shifts) |
| CdTe     | 50       | 6x6x6 (x4 shifts) |
| GaAs     | 40       | 6x6x6 (x4 shifts) |
| GaN      | 40       | 6x6x6 (x4 shifts) |
| GaP      | 40       | 6x6x6 (x4 shifts) |
| SiC      | 35       | 6x6x6 (x4 shifts) |
| ZnS      | 40       | 6x6x6 (x4 shifts) |
| ZnSe     | 40       | 6x6x6 (x4 shifts) |
| ZnTe     | 40       | 6x6x6 (x4 shifts) |
| BaO      | 40       | 8x8x8           |
| CaO      | 40       | 8x8x8           |
| Li2O     | 50       | 8x8x8           |
| MgO      | 50       | 8x8x8 (x4 shifts) |
| SrO      | 40       | 8x8x8           |

**TABLE S2**: Density functional theory calculated band parameters for triply degenerate valence bands given as Luttinger parameters, and non-degenerate anisotropic conduction bands given as electronic effective masses. In all calculation the theoretical lattice parameters were used, except for GaP where the experimental lattice parameter extrapolated at 0 K was used. The position of the band gap is also indicated.

| Material | cell(Bohr) | VB - Luttinger Param | CB - Eff. masses | Gap |
|----------|------------|----------------------|------------------|-----|
|          |            | A        | B         | C      | m_+   | m_-   |     |
| AlAs     | 10.825     | -4.681   | -1.019    | -5.498 | 0.243 | 0.897 | Γ-X  |
| AlN      | 8.130      | -1.435   | -0.351    | -1.793 | 0.321 | 0.520 | Γ-X  |
| AlP      | 10.406     | -2.598   | -0.894    | -3.335 | 0.252 | 0.809 | Γ-X  |
| AlSb     | 11.762     | -6.473   | -1.372    | -7.520 | 0.222 | 1.142 | Γ-L  |
| BAs      | 9.088      | -2.337   | -2.104    | -3.912 | 0.216 | 1.094 | Γ-Δ  |
| BN       | 6.746      | -0.917   | -0.969    | -1.635 | 0.299 | 0.895 | Γ-X  |
| CdS      | 11.202     | -3.999   | -0.605    | -4.321 | 0.118 | 0.118 | Γ-Γ  |
| CdSe     | 11.711     | -9.504   | -0.684    | -9.881 | 0.051 | 0.051 | Γ-Γ  |
| CdTe     | 12.513     | -9.517   | -0.867    | -10.033| 0.052 | 0.052 | Γ-Γ  |
| GaAs     | 10.863     | -54.896  | -1.362    | -55.859| 0.009 | 0.009 | Γ-Γ  |
| GaN      | 8.598      | -3.392   | -0.555    | -3.762 | 0.144 | 0.144 | Γ-X  |
| GaP      | 10.294     | -4.565   | -1.313    | -5.514 | 0.230 | 1.062 | Γ-Δ  |
| SiC      | 8.277      | -1.388   | -0.844    | -2.160 | 0.228 | 0.677 | Γ-X  |
| ZnS      | 10.286     | -2.751   | -0.694    | -3.170 | 0.167 | 0.167 | Γ-Γ  |
| ZnSe     | 10.833     | -5.340   | -0.791    | -5.834 | 0.089 | 0.089 | Γ-Γ  |
| ZnTe     | 11.682     | -6.495   | -1.032    | -7.174 | 0.076 | 0.076 | Γ-Γ  |
| BaO      | 10.566     | -0.216   | -2.018    | -2.018 | 0.380 | 1.197 | X-X  |
| CaO      | 9.121      | -1.407   | -0.174    | -0.653 | 0.443 | 1.424 | Γ-X  |
| Li2O     | 8.730      | -0.540   | -0.278    | -0.747 | 0.437 | 0.850 | Γ-X  |
| MgO      | 8.037      | -1.291   | -0.231    | -1.361 | 0.340 | 0.340 | Γ-Γ  |
| SrO      | 9.810      | -1.519   | -0.120    | -0.625 | 0.407 | 1.225 | Γ-X  |
TABLE S3: Calculated valence band ZPR for selected materials as in Miglio et al.\textsuperscript{1} in the generalized Fröhlich formalism ($ZPR_{gFr}$) based on first principles GGA-PBE parameters. The materials considered contain triply degenerated valence bands coupled to one LO phonon branch, except BaO which consist of only one electronic band. The lattice types abbreviations correspond to zinc-blende (zb), respectively rocksalt (rs) thus falling in the cubic space group symmetry.

| Material | Lattice | $\omega_{LO}$ (meV) | $\varepsilon_\infty$ | $\varepsilon_0$ | $ZPR_{gFr}$ (meV) |
|----------|---------|---------------------|---------------------|----------------|------------------|
| AlAs     | zb      | 47.3                | 9.49                | 11.51          | 11.50            |
| AlP      | zb      | 59.9                | 8.12                | 10.32          | 20.56            |
| AlSb     | zb      | 39.8                | 12.02               | 13.35          | 4.00             |
| BaS      | zb      | 84.4                | 9.81                | 9.89           | 0.53             |
| BN       | zb      | 161.0               | 4.52                | 6.69           | 94.47            |
| CdS      | zb      | 34.4                | 6.21                | 10.24          | 38.73            |
| CdSe     | zb      | 23.6                | 7.83                | 11.78          | 19.69            |
| CdTe     | zb      | 19.1                | 8.89                | 12.37          | 11.91            |
| GaAs     | zb      | 33.5                | 15.31               | 17.55          | 3.26             |
| GaN      | zb      | 86.0                | 6.13                | 16.30          | 72.26            |
| GaP      | zb      | 48.6                | 10.50               | 11.00          | 8.46             |
| SiC      | zb      | 117.0               | 6.97                | 10.30          | 58.28            |
| ZnS      | zb      | 40.6                | 5.97                | 9.40           | 40.06            |
| ZnSe     | zb      | 29.3                | 7.35                | 10.73          | 21.69            |
| ZnTe     | zb      | 24.1                | 9.05                | 11.99          | 11.06            |
| BaO      | rs      | 47.3                | 4.21                | 92.43          | 225.34           |
| CaO      | rs      | 66.8                | 3.77                | 16.76          | 223.20           |
| Li\textsubscript{2}O | rs | 86.3                | 2.9                 | 7.8            | 364.59           |
| MgO      | rs      | 84.5                | 3.23                | 11.14          | 326.99           |
| SrO      | rs      | 55.4                | 3.77                | 20.91          | 228.95           |

TABLE S4: Convergence sampling used in the calculation of the self-energy term in the degenerate band scenario for 19 of the studied materials. $\partial^2 \Sigma / \partial k^2$ was converged until a $1E - 5$ Ha precision was reached.

| Material | 100 | 110 | 111 |
|----------|-----|-----|-----|
| AlAs     | 240 | 240 | 240 |
| AlP      | 144 | 144 | 144 |
| AlSb     | 240 | 240 | 240 |
| BaS      | 128 | 128 | 128 |
| BN       | 240 | 240 | 240 |
| CdS      | 320 | 320 | 320 |
| CdSe     | 360 | 360 | 360 |
| CdTe     | 360 | 360 | 360 |
| GaAs     | 320 | 320 | 320 |
| GaN      | 320 | 320 | 320 |
| GaP      | 280 | 280 | 280 |
| SiC      | 160 | 160 | 160 |
| ZnS      | 280 | 280 | 280 |
| ZnSe     | 240 | 240 | 240 |
| ZnTe     | 280 | 280 | 280 |
| CaO      | 360 | 360 | 360 |
| Li\textsubscript{2}O | 280 | 280 | 280 |
| MgO      | 320 | 320 | 320 |
| SrO      | 400 | 400 | 400 |

1 A. Miglio, V. Brousseau-Couture, E. Godbout, G. Antonius, Y.-H. Chan, S. G. Louie, M. Côté, M. Giantomassi, and X. Gonze, npj Computational Materials 6, 167 (2020).
TABLE S5: Second order derivative of the self-energy with respect to the wave-vector along different high-symmetry directions relevant to cubic materials. The quantity is calculated via a finite difference method around \(k = 0\). The quantities are expressed in atomic units.

| Material | \(\partial^2 \Sigma / \partial k^2\) (100) | \(\partial^2 \Sigma / \partial k^2\) (110) | \(\partial^2 \Sigma / \partial k^2\) (111) |
|----------|---------------------------------|---------------------------------|---------------------------------|
| AlAs     | 0.778                           | 0.112                           | 0.908                           |
| AlP      | 0.574                           | 0.164                           | 0.732                           |
| AlSb     | 0.442                           | 0.078                           | 0.512                           |
| BaS      | 0.008                           | 0.006                           | 0.014                           |
| BN       | 0.283                           | 0.267                           | 0.259                           |
| CdS      | 3.092                           | 0.390                           | 3.394                           |
| CdSe     | 6.059                           | 0.416                           | 6.330                           |
| CdTe     | 4.422                           | 0.366                           | 4.685                           |
| GaAs     | 4.596                           | 0.149                           | 4.671                           |
| GaN      | 2.086                           | 0.286                           | 2.324                           |
| GaP      | 0.510                           | 0.120                           | 0.620                           |
| SiC      | 0.431                           | 0.224                           | 0.656                           |
| ZnS      | 1.732                           | 0.353                           | 2.038                           |
| ZnSe     | 2.762                           | 0.345                           | 3.040                           |
| ZnTe     | 2.072                           | 0.276                           | 2.300                           |
| CaO      | 2.551                           | 0.176                           | 2.019                           |
| Li2O     | 1.342                           | 0.574                           | 1.893                           |
| MgO      | 3.231                           | 0.461                           | 3.557                           |
| SrO      | 3.592                           | 0.146                           | 2.670                           |

TABLE S6: Inverse of hole polaron effective masses associated with the triply degenerate valence bands along different crystallographic directions. The quantities are expressed in atomic units.

| Material | \(1/m^*_\text{pol}(100)\) | \(1/m^*_\text{pol}(110)\) | \(1/m^*_\text{pol}(111)\) |
|----------|------------------------|------------------------|------------------------|
| AlAs     | -5.853                 | -1.897                 | -10.290                |
| AlP      | -6.821                 | -1.623                 | -6.095                 |
| AlSb     | -12.503                | -2.667                 | -14.853                |
| BaS      | -4.666                 | -4.202                 | -8.339                 |
| BN       | -1.551                 | -1.672                 | -2.983                 |
| CdS      | -4.906                 | -0.821                 | -5.531                 |
| CdSe     | -12.949                | -0.951                 | -13.738                |
| CaO      | -14.612                | -1.367                 | -15.735                |
| GaAs     | -105.195               | -2.576                 | -107.445               |
| GaN      | -6.819                 | -0.824                 | -5.386                 |
| GaP      | -7.370                 | -1.936                 | -3.736                 |
| SiC      | -3.770                 | -1.936                 | -4.577                 |
| ZnS      | -7.917                 | -1.237                 | -8.925                 |
| ZnSe     | -10.918                | -1.787                 | -12.400                |
| ZnTe     | -10.918                | -1.787                 | -12.400                |
| BaO      | -0.108                 | -0.108                 | -0.108                 |
| CaO      | -0.262                 | -0.171                 | -0.215                 |
| Li2O     | 0.261                  | 0.019                  | 0.327                  |
| MgO      | 0.648                  | -0.002                 | 0.673                  |
| SrO      | 0.555                  | -0.094                 | 0.415                  |
TABLE S7: Ratio between the electronic effective mass and polaron effective mass along different directions in the studied cubic materials characteristic to the degenerate electronic bands case.

| Material | $m_e/m_{pol}(100)$ | $m_e/m_{pol}(110)$ | $m_e/m_{pol}(111)$ |
|----------|---------------------|---------------------|---------------------|
| AlAs     | 0.917               | 0.931               | 0.931               |
| AIP      | 0.889               | 0.908               | 0.908               |
| AlSb     | 0.966               | 0.972               | 0.972               |
| BAs      | 0.998               | 0.999               | 0.999               |
| BN       | 0.846               | 0.862               | 0.862               |
| CdS      | 0.613               | 0.678               | 0.678               |
| CdSe     | 0.681               | 0.696               | 0.696               |
| CdTe     | 0.706               | 0.789               | 0.789               |
| GaAs     | 0.958               | 0.945               | 0.945               |
| GaN      | 0.693               | 0.742               | 0.742               |
| GaP      | 0.944               | 0.954               | 0.954               |
| SiC      | 0.845               | 0.867               | 0.867               |
| ZnS      | 0.685               | 0.746               | 0.746               |
| ZnSe     | 0.741               | 0.782               | 0.782               |
| ZnTe     | 0.840               | 0.866               | 0.866               |
| BaO      | 0.436               | 0.436               | 0.436               |
| CaO      | 0.093               | 0.493               | 0.493               |
| Li2O     | -0.24               | -0.034              | -0.034              |
| MgO      | -0.251              | 0.003               | -0.233              |
| SrO      | -0.183              | 0.391               | -0.183              |

TABLE 8.a: Hole polaron localization length determined in the studied materials along different high-symmetry directions relevant to cubic materials pertaining to the degenerate electronic bands case. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell. The lengths are expressed as a function of the repetition distance between equivalent atoms in the unit cell.

| Material | (100) | (110) | (111) | d(Bohr) |
|----------|-------|-------|-------|---------|
| AlAs     | 136.43| 78.53 | 78.53 | 7.654   |
| AIP      | 65.69 | 44.70 | 44.70 | 7.358   |
| AlSb     | 383.71| 218.69| 218.69| 8.317   |
| BAs      | 3171.4| 3054.4| 3054.4| 6.426   |
| BN       | 69.13 | 39.75 | 39.75 | 4.770   |
| CdS      | 29.04 | 14.56 | 14.56 | 7.921   |
| CdSe     | 46.91 | 24.07 | 24.07 | 8.281   |
| CdTe     | 76.98 | 65.88 | 65.88 | 8.488   |
| GaAs     | 1797.95| 455.74| 455.74| 7.681   |
| GaN      | 28.82 | 14.93 | 14.93 | 6.080   |
| GaP      | 185.63| 118.34| 118.34| 7.279   |
| SiC      | 31.24 | 26.13 | 26.13 | 7.279   |
| ZnS      | 29.64 | 16.37 | 16.37 | 5.853   |
| ZnSe     | 38.64 | 29.27 | 29.27 | 6.173   |
| ZnTe     | 107.15| 54.89 | 54.89 | 8.260   |
| CaO      | 3.60  | 1.68  | 1.68  | 6.450   |
| Li2O     | 2.31  | 1.82  | 1.82  | 6.173   |
| MgO      | 3.98  | 2.13  | 2.13  | 5.683   |
| SrO      | 2.92  | 1.15  | 1.15  | 6.937   |
TABLE 8.b: Hole polaron formation energy in the strong coupling limit along different high-symmetry directions relevant to cubic materials pertaining to the degenerate electronic bands case.

| Material | $E_{SC}$(meV) | (100) | (110) | (111) |
|----------|--------------|-------|-------|-------|
| AlAs     | -0.13517     | -0.20604 | -0.19736 |
| AlP      | -0.37606     | -0.57906 | -0.54229 |
| AlSb     | -0.01994     | -0.02958 | -0.02875 |
| BAs      | -0.00023     | -0.00031 | -0.00029 |
| BN       | -3.90519     | -5.22358 | -4.90517 |
| CdS      | -2.27488     | -3.01849 | -3.07203 |
| CdSe     | -0.64406     | -0.85738 | -0.87593 |
| CdTe     | -0.31171     | -0.42327 | -0.43000 |
| GaAs     | -0.00694     | -0.00960 | -0.00966 |
| GaN      | -3.33710     | -4.69221 | -4.68922 |
| GaP      | -0.08218     | -0.11823 | -0.11551 |
| SiC      | -1.54667     | -2.56839 | -2.20181 |
| ZnS      | -2.30872     | -3.13410 | -3.14241 |
| ZnSe     | -0.78833     | -1.08677 | -1.09486 |
| ZnTe     | -0.24936     | -0.34915 | -0.34901 |
| CaO      | -75.87667    | -62.73596 | -57.15204 |
| Li2O     | -96.31797    | -137.12446 | -131.20188 |
| MgO      | -77.31154    | -95.18113 | -97.82699 |
| SrO      | -101.31612   | -75.53183 | -64.65848 |

TABLE S9: Electron polaron localization length expressed in units of the repetition distance between equivalent atoms. $a_p(d)$ is the spherical average determined by Eq. 108 where the electronic effective masses expressed in Table S2 have been used. $a_{p\perp}$ is the in-plane localization length. $a_{pz}$ is the out-of-plane localization length. The radii are determined in the Fröhlich model.

| Material | $a_p(d)$ | $a_{p\perp}(d)$ | $a_{pz}(d)$ | Ratio | Shape |
|----------|----------|-----------------|-------------|-------|-------|
| AlAs     | 13.81    | 16.10           | 10.15       | 0.63  | oblate |
| AlN      | 28.70    | 30.39           | 25.59       | 0.84  | oblate |
| AlP      | 12.04    | 13.81           | 9.14        | 0.66  | oblate |
| AlSb     | 18.92    | 22.94           | 12.87       | 0.56  | oblate |
| BAs      | 259.24   | 313.63          | 177.12      | 0.56  | oblate |
| BN       | 6.37     | 7.25            | 4.92        | 0.68  | oblate |
| CdS      | 63.62    | -               | -           | -     | spherical |
| CdSe     | 207.27   | -               | -           | -     | spherical |
| CdTe     | 259.36   | -               | -           | -     | spherical |
| GaAs     | 6439.74  | -               | -           | -     | spherical |
| GaN      | 59.65    | 59.65           | 59.65       | 1.00  | spherical |
| GaP      | 13.15    | 15.75           | 9.17        | 0.58  | oblate |
| SiC      | 10.67    | 12.14           | 8.26        | 0.68  | oblate |
| ZnS      | 50.60    | -               | -           | -     | spherical |
| ZnSe     | 128.23   | -               | -           | -     | spherical |
| ZnTe     | 219.80   | -               | -           | -     | spherical |
| BaO      | 1.09     | 1.24            | 0.83        | 0.67  | oblate |
| CaO      | 1.04     | 1.19            | 0.79        | 0.66  | oblate |
| Li2O     | 2.37     | 2.57            | 2.03        | 0.79  | oblate |
| MgO      | 7.26     | -               | -           | -     | spherical |
| SrO      | 0.98     | 1.11            | 0.75        | 0.68  | oblate |
TABLE S10: Electron polaron localization length expressed in units of the repetition distance between equivalent atoms. $a_p(d)$ is the spherical average determined by Eq. 37 where the electronic effective masses expressed in Table S2 have been used. $a_{p\perp}$ is the in-plane localization length. $a_{pz}$ is the out-of-plane localization length. The radii are determined in the Feynman model.

| Material | $a_p(d)$ | $a_{p\perp}(d)$ | $a_{pz}(d)$ | Ratio | Shape |
|----------|----------|-----------------|-------------|-------|-------|
| AlAs     | 16.72    | 28.72           | 5.66        | 0.20  | oblate|
| AlP      | 13.96    | 22.64           | 5.31        | 0.23  | oblate|
| AlSb     | 23.26    | 45.97           | 5.96        | 0.13  | oblate|
| BAs      | 81.55    | 160.16          | 21.14       | 0.13  | oblate|
| BN       | 8.57     | 13.47           | 3.47        | 0.26  | oblate|
| CdS      | 40.82    | -               | -           | -     | spherical|
| CdSe     | 146.15   | -               | -           | -     | spherical|
| CdTe     | 164.80   | -               | -           | -     | spherical|
| GaAs     | 2783.85  | -               | -           | -     | spherical|
| GaN      | 30.76    | -               | -           | -     | spherical|
| GaP      | 18.62    | 35.14           | 5.23        | 0.15  | oblate|
| SiC      | 13.11    | 20.55           | 5.33        | 0.26  | oblate|
| ZnS      | 28.07    | -               | -           | -     | spherical|
| ZnSe     | 74.74    | -               | -           | -     | spherical|
| ZnTe     | 110.51   | -               | -           | -     | spherical|
| BaO      | 3.36     | 5.34            | 1.32        | 0.25  | oblate|
| CaO      | 3.03     | 4.86            | 1.18        | 0.24  | oblate|
| Li2O     | 3.58     | 4.68            | 2.09        | 0.45  | oblate|
| MgO      | 6.91     | -               | -           | -     | spherical|
| SrO      | 3.30     | 5.15            | 1.35        | 0.26  | oblate|

TABLE S11: Calculated conduction band ZPR for selected materials as in Miglio et al\textsuperscript{11} in the generalized Fröhlich formalism ($ZPR^F_{Fr}$) based on first principles GGA-PBE parameters and compared to the Feynman variational approach for both isotropic and anisotropic non-degenerate electronic bands.

| Material | Fröhlich $ZPR^F_{Fr}$ (meV) | Feynman $F_{avg}$ (meV) | $F_{z}$ (meV) | $F_{\perp}$ (meV) | R.E. (%) |
|----------|-------------------------------|------------------------|--------------|------------------|---------|
| AlAs     | -8.8                          | -9.6                   | -7.3         | -14.1            | -9.4%   |
| AlP      | -14.0                         | -15.1                  | -11.9        | -21.4            | -7.6%   |
| AlSb     | -3.6                          | -4.1                   | -2.9         | -6.5             | -15.0%  |
| BAs      | -0.5                          | -0.6                   | -0.4         | -0.9             | -14.2%  |
| BN       | -67.9                         | -72.6                  | -58.3        | -101.3           | -7.0%   |
| CdS      | -14.9                         | -15.0                  | -15.0        | -15.0            | -0.5%   |
| CdSe     | -5.5                          | -5.5                   | -5.5         | -5.5             | -0.3%   |
| CdTe     | -3.7                          | -3.7                   | -3.7         | -3.7             | -0.3%   |
| GaAs     | -0.5                          | -0.5                   | -0.5         | -0.5             | 0.4%    |
| GaN      | -29.6                         | -29.7                  | -29.7        | -29.7            | -0.4%   |
| GaP      | -7.4                          | -8.3                   | -6.0         | -13.0            | -13.0%  |
| SiC      | -32.7                         | -34.8                  | -28.0        | -48.4            | -6.6%   |
| ZnS      | -18.6                         | -18.7                  | -18.7        | -18.7            | -0.6%   |
| ZnSe     | -8.1                          | -8.1                   | -8.1         | -8.1             | -0.3%   |
| ZnTe     | -4.3                          | -4.3                   | -4.3         | -4.3             | -0.2%   |
| BaO      | -132.0                        | -148.2                 | -115.9       | -212.7           | -12.3%  |
| CaO      | -153.9                        | -171.2                 | -133.7       | -246.1           | -11.3%  |
| Li2O     | -171.7                        | -180.8                 | -159.1       | -224.2           | -5.3%   |
| MgO      | -137.3                        | -140.4                 | -140.4       | -140.4           | -2.2%   |
| SrO      | -141.0                        | -156.5                 | -124.1       | -221.3           | -11.0%  |
TABLE S12: Calculated conduction band polaron effective masses for selected materials as in Miglio et al. in the generalized cubic Fröhlich formalism based on first principles GGA-PBE parameters and compared to the Feynman variational approach for both isotropic and anisotropic non-degenerate electronic bands.

| Material | Fröhlich | Feynman | R.E. |
|----------|----------|----------|------|
|          | $m_{\text{pol}}^\| [\text{a.u.}]$ | $m_{\text{pol}}^\perp [\text{a.u.}]$ | $m_{\text{pol}}^\| [\text{a.u.}]$ | $m_{\text{pol}}^\perp [\text{a.u.}]$ | $m_{\text{pol}}^\| / m_{\text{pol}}^\perp$ [\text{a.u.}] | $m_{\text{pol}}^\perp / m_{\text{pol}}^\|$ [\text{a.u.}] |      |
| AlAs     | 0.25181  | 0.91550  | 0.24901 | 0.94087 | 1.1%   | -2.8%  |      |
| AlP      | 0.26372  | 0.83222  | 0.26024 | 0.85736 | 1.3%   | -3.0%  |      |
| AlSb     | 0.2561   | 1.15212  | 0.22422 | 1.17299 | 0.6%   | -1.8%  |      |
| BAs      | 0.21668  | 1.09474  | 0.21660 | 1.09608 | 0.0%   | -0.1%  |      |
| BN       | 0.32467  | 0.94301  | 0.31661 | 0.98838 | 2.5%   | -4.8%  |      |
| CdS      | 0.12688  | 0.12688  | 0.12622 | 0.12622 | 0.5%   | 0.5%   |      |
| CdSe     | 0.05322  | 0.05322  | 0.05313 | 0.05313 | 0.2%   | 0.2%   |      |
| CdTe     | 0.05349  | 0.05349  | 0.05344 | 0.05344 | 0.1%   | 0.1%   |      |
| GaAs     | 0.00914  | 0.00914  | 0.00914 | 0.00914 | 0.0%   | 0.0%   |      |
| GaN      | 0.15229  | 0.15228  | 0.15179 | 0.15179 | 0.3%   | 0.3%   |      |
| GaP      | 0.23670  | 1.07856  | 0.23431 | 1.10864 | 1.0%   | -2.8%  |      |
| SiC      | 0.24000  | 0.70067  | 0.23723 | 0.72354 | 1.5%   | -3.3%  |      |
| ZnS      | 0.18094  | 0.18094  | 0.17989 | 0.17989 | 0.6%   | 0.6%   |      |
| ZnSe     | 0.09362  | 0.09362  | 0.09343 | 0.09343 | 0.2%   | 0.2%   |      |
| ZnTe     | 0.07877  | 0.07877  | 0.07871 | 0.07871 | 0.1%   | 0.1%   |      |
| BaO      | 0.81412  | 1.78651  | 0.53076 | 2.03669 | 34.8%  | -14.0% |      |
| CaO      | 0.79178  | 1.95175  | 0.58676 | 2.25401 | 25.9%  | -15.5% |      |
| Li2O     | 0.68378  | 1.17113  | 0.56847 | 1.20511 | 16.9%  | -2.9%  |      |
| MgO      | 0.46571  | 0.46571  | 0.43153 | 0.43153 | 7.3%   | 7.3%   |      |
| SrO      | 0.78801  | 1.76349  | 0.55448 | 1.99554 | 29.6%  | -13.2% |      |

TABLE S13: Feynman path integral variational method parameters for the non-degenerate anisotropic case.

| Materials | $v_\perp$ | $w_\perp$ | $v_\| $ | $w_\|$ |
|-----------|-----------|-----------|--------|--------|
| AlAs      | 3.01564   | 2.98092   | 3.03038 | 2.96301 |
| AlP       | 3.02014   | 2.97542   | 3.03662 | 2.95554 |
| AlSb      | 3.00726   | 2.99193   | 3.01659 | 2.97079 |
| BAs       | 3.00054   | 2.99946   | 3.00569 | 3.00569 |
| BN        | 3.03711   | 2.95497   | 3.05888 | 2.92992 |
| CdS       | 3.04481   | 2.94577   | 3.04812 | 2.94576 |
| CdSe      | 3.02365   | 2.97114   | 3.02366 | 2.97114 |
| CdTe      | 3.01560   | 2.97622   | 3.01949 | 2.97621 |
| GaAs      | 3.00178   | 2.99821   | 3.00474 | 3.00117 |
| GaN       | 3.03337   | 2.95703   | 3.03337 | 2.95703 |
| GaP       | 3.01381   | 2.98008   | 3.02114 | 2.96694 |
| SiC       | 3.02434   | 2.97036   | 3.04256 | 2.94843 |
| ZnS       | 3.04752   | 2.94256   | 3.04751 | 2.94255 |
| ZnSe      | 3.02819   | 2.96567   | 3.02819 | 2.96567 |
| ZnTe      | 3.01804   | 2.97800   | 3.01805 | 2.97801 |
| BaO       | 3.03498   | 2.66690   | 3.72792 | 3.23291 |
| CaO       | 3.23770   | 2.73342   | 3.53099 | 2.46877 |
| Li2O      | 3.21540   | 2.75629   | 3.32837 | 2.64464 |
| MgO       | 3.19076   | 2.78207   | 3.19075 | 2.78206 |
| SrO       | 3.27253   | 2.69853   | 3.60088 | 3.41346 |
TABLE S14: Cs$_2$NaScF$_6$ hole and electron polaron characteristics, respectively effective masses and localization lengths, along 3 crystallographic directions.

| Luttinger Parameters | 0.02891 | 0.07544 | 0.00377 |
|----------------------|---------|---------|---------|
|                       |         |         |         |
| CB electron effective mass |
| (100) 17.293 | 6.628   | 6.628   |
| (110) 9.942 | 9.942   | 6.628   |
| (111) 8.521 | 8.521   | 8.007   |
| Electron polaron effective mass |
| (100) -11.992 | -2.518  | -2.518  |
| (110) -3.399 | -3.399  | -2.518  |
| (111) -3.522 | -3.522  | -3.227  |
| Localization length (d) |
| (100) | 0.16 | 0.23 | 0.23 |
| (110) | 0.20 | 0.20 | 0.23 |
| (111) | 0.22 | 0.22 | 0.22 |
| $E_{SC}$ (meV) |
| (100) | -1365.54 |
| (110) | -1299.45 |
| (111) | -1284.82 |

| Luttinger parameters | -0.00205 | -0.08035 | -0.01328 |
|----------------------|----------|----------|----------|
|                       |          |          |          |
| VB electron effective mass |
| (100) -243.704 | -6.223  | -6.223  |
| (110) -14.467 | -10.451 | -6.223  |
| (111) -10.035 | -10.035 | -7.923  |
| Hole polaron effective mass |
| (100) 1.417 | 1.417   | 265.341 |
| (110) 1.417 | 2.382   | 3.452   |
| (111) 1.791 | 2.335   | 2.335   |
| Localization length (d) |
| (100) | 0.05 | 0.17 | 0.17 |
| (110) | 0.16 | 0.18 | 0.22 |
| (111) | 0.19 | 0.19 | 0.21 |
| $E_{SC}$ (meV) |
| (100) | -2222.08 |
| (110) | -1483.25 |
| (111) | -1425.88 |

| Dielectric coupling |
|---------------------|----------|----------|
| Mode | Frequency | $\epsilon'$ |
|------|----------|------------|
| 12   | 13.05    | 36.64      |
| 18   | 22.94    | 11.03      |
| 24   | 31.98    | 20.43      |
| 30   | 57.77    | 6.26       |