Model Pseudopotentials for Color Centers

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Abstract. The energy-dependent pseudopotentials for electron-excess color centers in ionic crystals adopted by Bartram, Stoneham and Gash (BSG) were determined by a smoothness criterion because the trial wave functions employed are slowly varying on the scale of the ion cores. Energy-independent norm-conserving pseudopotentials were introduced subsequently in the context of molecular-orbital calculations to ensure that the outer parts of valence pseudo-orbitals coincide with those of true valence orbitals. In the present investigation, whole-ion norm-conserving pseudopotentials calculated from numerical wave functions are employed in \textit{F}-center calculations for comparison with BSG calculations. It is concluded that the smoothness criterion should take precedence in that application.

1. Introduction

Energy-dependent whole-ion pseudopotentials for electron-excess color centers were introduced by Bartram, Stoneham and Gash (BSG) [1] to address ion-size effects in alkali–halide \textit{F}-band energies observed by Buchenauer and Fitchen (BF) [2] as systematic departures from the Ivey law [3]. These pseudopotentials were predicated on a smoothness criterion since the trial wave functions employed for electron-excess color centers are slowly varying on the scale of the ion cores. Energy-independent norm-conserving pseudopotentials were introduced subsequently in the context of molecular-orbital calculations on covalent complexes to ensure that the outer parts of valence pseudo-orbitals coincide with those of true valence orbitals [4], [5]. In the present investigation, energy-independent whole-ion norm-conserving pseudopotentials calculated from numerical wave functions [6], stabilized for anions by Watson wells [7], are employed in \textit{F}-center calculations for comparison with corresponding BSG calculations [1], with the point-ion (PI) calculations of Gourary and Adrian [8] and with the BF experimental values [2].

2. BSG Pseudopotentials

The energy-dependent pseudopotentials introduced by BSG [1] were expressed in the form

\[ V_p = V_{pI} + \sum \gamma C_{\gamma} \delta(\vec{r} - \vec{r}_{\gamma}) , \] (1)

where \( V_{pI} \) is the point-ion potential [8] and the pseudopotential coefficient \( C_{\gamma} \) for ion \( \gamma \) is given by...
\[ C_\gamma = A_\gamma + (V - U_\gamma)B_\gamma, \quad (2a) \]
\[ A_\gamma = \int [(1 - P_\gamma)(V_\gamma - V_{p\gamma}) - \int P_\gamma V_{p\gamma}d\tau, \quad (2b) \]
\[ B_\gamma = \int P_\gamma d\tau, \quad (2c) \]
\[ \overline{V} = (\phi, V_\mu \phi)/(\phi, \phi), \quad (2d) \]
\[ U_\gamma = \sum_{\mu \neq \gamma} V_{p\mu}, \quad (2e) \]

where \( P_\gamma \) is a projection operator for the core orbitals of ion \( \gamma \). The average value of the pseudopotential \( \overline{V} \) was replaced by the total energy \( E \) in subsequent applications [9]; they are equivalent in the limit of smooth trial functions.

3. Norm-Conserving Pseudopotentials

The relevant equations for norm-conserving whole-ion pseudopotentials for monovalent ions are:

\[ U(r) = \varepsilon_l - \frac{l(l+1)}{2r^2} + \frac{Z}{r} + \frac{\phi''(r)}{2\phi_l(r)} - V(r), \quad (3) \]

\[ V_\gamma(r) = \frac{Q_{\gamma\text{well}}}{r_{\gamma\text{well}}} + Q_{\gamma\text{well}} \left( \frac{1}{r_{\gamma\text{well}}} - \frac{1}{r} \right) \theta(r - r_{\gamma\text{well}}) \quad \text{(anions)}, \quad (4a) \]

\[ V_\gamma(r) = 0 \quad \text{(cations)}, \quad (4b) \]

\[ \phi_l(r) = \sum_{n=0}^4 a_n^{(l)} r^{l+n+3}, \quad r < r_c, \quad (5a) \]

\[ \phi_l(r) = \psi_l(r), \quad r > r_c. \quad (5b) \]

The matching conditions at \( r = r_c \leq r_{\gamma\text{well}} \) can be expressed in the form

\[ \sum_{n=0}^4 A_l^{(l)} = \psi_l(r_c), \quad (6a) \]

\[ \sum_{n=0}^4 (l+n+3)A_l^{(l)} = r_c \psi_l'(r_c), \quad (6b) \]

\[ \sum_{n=0}^4 (l+n+3)(l+n+2)A_l^{(l)} = r_c^2 \psi_l''(r_c), \quad (6c) \]
\[
\sum_{n=0}^{4} (l + n + 3)(l + n + 2)(l + n + 1)A_n^{(l)} = r_c^3 \psi^{(m)}(r_c),
\]

where \( A_n^{(l)} \) is defined by
\[
A_n^{(l)} = A_n^{(l)} r_c^{l+n+3}.
\]

Thus Equations (6) comprise four linear algebraic equations in the five unknown quantities \( A_n^{(l)} \); by matrix inversion, one obtains solutions in the form
\[
A_n^{(l)} = W_n^{(l)} + \beta_n^{(l)} A_0^{(l)}, \quad 0 < n \leq 4.
\]

A fifth relation is provided by the normalization condition,
\[
N^{(l)} = 1 - \int_0^\infty \psi_l(r)^2 dr = \int_0^\infty \phi_l(r)^2 dr = r_c \sum_{m+n=0}^{4} \frac{A_m^{(l)} A_n^{(l)}}{m+n+7+2l}.
\]

An example of a numerical wave function for \( l = 0 \) together with the corresponding norm-conserving pseudowavefunction is presented in Figure 1 for \( \text{Cl}^2^- \). In each case, the matching radius \( r_c \) was chosen to coincide with the maximum of the outer lobe of \( \psi_0(r) \). For anions, the radius \( r_{\text{well}} \) was specified as \(~1.75\) times the ionic radius and the charge \( Q_{\text{well}} \) was chosen to make the well depth 1.0 Hartree in each case.

![Wavefunction](image.png)

Figure 1. Numerical wave function \( \psi(r) \) for \( \text{Cl}^2^- \) in a Watson well, together with the corresponding norm-conserving pseudowavefunction \( \phi(r) \).

Finally, the energy-independent pseudopotential coefficient \( C_\gamma \) is given by
The calculated norm-conserving pseudopotentials for monovalent anions and cations are plotted in Figures 2 and 3, respectively.

\[
C_\gamma = 4\pi \int_0^\infty \left[ U_0(r) - \frac{Z}{r} + \frac{Q_{\text{norm}}}{r} \right] r^2 dr = \left[ \epsilon_0 - V_\epsilon(r) \right] \frac{4\pi r^3}{3} + 2\pi Q_{\text{norm}} r^2
\]

\[
+ 2\pi \int_0^\infty \left[ \sum_{n=0}^4 (n+3)(n+2) a_n^{(0)} r^n \right] dr + 4\pi \int_0^\infty \frac{\psi_{\text{ion}}'(r)}{2\psi_0(r)} r^2 dr.
\]

(10)

The integrand of pseudopotential coefficient \( C_\gamma \) as a function of \( r \) for halogen ions.

![Figure 2](image2.png)

Figure 2. The integrand of pseudopotential coefficient \( C_\gamma \) as a function of \( r \) for halogen ions.

The integrand of pseudopotential coefficient \( C_\gamma \) as a function of \( r \) for alkali ions.

![Figure 3](image3.png)

Figure 3. The integrand of pseudopotential coefficient \( C_\gamma \) as a function of \( r \) for alkali ions.
4. **F-Center Calculations**

F-center transition energies incorporating ion-size corrections based on norm-conserving pseudopotentials (NCP) were calculated for the seventeen alkali halides with rock-salt structure. The required input data are listed in Table I.

| Ion | $C_r$ (Hartree $a_0^3$) | $A_{H} + A_{X}$ (Rydberg $a_0^3$) | $B$ ($a_0^3$) |
|-----|-----------------|-----------------|---------|
| F^- | 26.45           | 52.90           | 0.0     |
| Cl^- | -50.42          | -100.84         | 0.0     |
| Br^- | 26.07           | 52.14           | 0.0     |
| I^-  | 34.61           | 69.22           | 0.0     |
| Li^+ | 36.40           | 72.80           | 0.0     |
| Na^+ | 44.76           | 89.52           | 0.0     |
| K^+  | 77.85           | 155.70          | 0.0     |
| Rb^+ | 94.05           | 188.10          | 0.0     |
| Cs^+ | 127.08          | 254.16          | 0.0     |

Calculations were performed by the method of BSG [1] which proceeds from the PI method [8] augmented by corrections for ion-size effects, polarization and distortion. The ion-size correction employed by BSG was diminished by an adjustable parameter $\alpha$. Ion-size corrections based on the NCP coefficients listed in Table I, similarly diminished, were employed in the present work. Calculated $F$-band energies, normalized to the Ivey law [3], are compared in Figure 4 with the experimental results of BF [2].

![Figure 4](image-url)  
**Figure 4.** $F$-band energies normalized to the Ivey law [3]. White squares denote the experimental values of BF [2], the continuous curve is a plot of Equation (11), red diamonds represent the PI approximation [8] with corrections for polarization and distortion, black circles include the BSG [1] ion-size correction as well and green triangles include instead an ion-size correction based on the NCP coefficients $C_r$ listed in Table I. Ion-size corrections are diminished by an adjustable parameter $\alpha$ and $Dev$ is the sum of squares of energy differences, in Rydbergs, between theory and experiment.

The continuous curve is a saturating exponential fitted to the experimental data, given by

$$\frac{\Delta E(a,R)}{\Delta E_{Ivey}(a)} = 1.05 - 18.0 \exp(-5.5R), \quad (11)$$
\[ \Delta E_{\text{Ivey}}(a) = 4.18a^{-1.84}, \]  

(12)

where \( a \) is the nearest-neighbor distance in atomic units and \( R \) is the ratio of ionic radii,

\[ a \equiv r_{\text{anion}} + r_{\text{cation}} , \]  

(13)

\[ R \equiv r_{\text{anion}} / r_{\text{cation}} . \]  

(14)

5. Discussion

Energy-independent norm-conserving pseudopotentials were introduced as a formal device for application of the frozen-core approximation in molecular calculations and are still extensively employed for that purpose. However, it is evident from Figure 4 that whole-ion NCP’s are inferior to the BSG pseudopotentials for calculating ion-size corrections to \( F \)-band energies, since the required reduction factor \( \alpha \) is much smaller and their deviation from experiment is significantly greater. In particular, the calculation fails to reproduce the observed dependence of ion-size effects on the ratio of ionic radii [2]. Figure 1-3 illustrate the fact that norm conservation can be achieved only by imposition of a pseudopotential that is highly repulsive at the ion core and is thus incompatible with a smooth trial function. On the other hand, norm-conservation is essentially irrelevant for electron-excess color centers where covalent bonding is not involved.

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