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Application of the chemical pseudopotential method to the calculation of the energy band structure of CuI v

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Abstract. The band structure of CuI v (a tetragonal phase under pressure) is calculated by applying the chemical pseudopotential method. The estimation of the energy gap is given and the results are compared to the previous linear muffin-tin orbital calculation. The spin-orbit interaction effects are taken into consideration. The paper also points out to some important limitations of the chemical pseudopotential method.

1. Introduction

Recently Blacha *et al* [1] have reported results of measurements of optical-absorption spectra of thin films of copper halides (CuCl, CuI and CuBr) for pressures between 0 and 10 GPa. In this interval the copper halides undergo a number of structural phase transitions [2]. On the basis of appropriate considerations they observed that, in tetragonal phases of CuI and CuCl, the absorption peaks can be assigned to the edge excitons at the Γ point ($k = 0$ in the Brillouin zone (BZ)) related to the electrons in the lowest conduction band and the holes in the highest valence bands. They performed band-structure calculations by the fully relativistic, self-consistent (SC) linear muffin-tin orbital (LMTO) method but their results for absorption edges are lower than the experimental exciton energies. For example, the energy gap between the highest valence band and the lowest conduction band at the Γ point for CuI v (tetragonal phase) is 1.3 eV, i.e. less than half the experimental gap of 2.92 eV [3]. This is an expected consequence of the local-density approximation applied in the LMTO method [4].

Here, the energy band structure of CuI v is given on the basis of the chemical pseudopotential method [5], which appears to be quite useful in the tight-binding analysis of energy bands [6]. The purpose of this paper is to estimate the energy gap of CuI v within this method. In § 2 the crystal structure and group-theoretical analysis are presented. In §§ 3 and 4 the results of the calculation are given and some of this chemical pseudopotential method's limitations are pointed out. The conclusions are given in § 5.

However, CuCl is not treated because of uncertainties in crystallographic structure in the tetragonal phase of this compound [1].

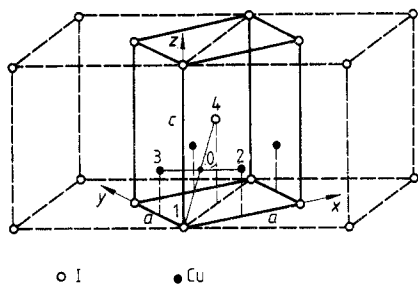


Figure 1. Unit cell of the tetragonal PbO structure of CuI v. The positions of the atoms within the unit cell are given in the text. $a = 4.02 \text{ \AA}$, $c = 5.70 \text{ \AA}$.

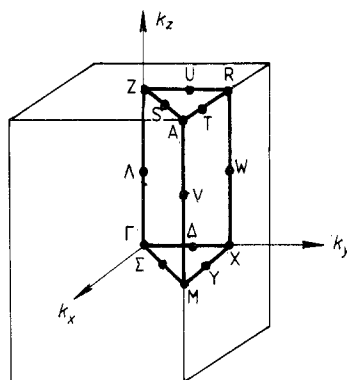


Figure 2. The first Brillouin zone shown with symmetry points and lines.

2. The crystal structure and the group-theoretical analysis

CuI v has the PbO structure, shown in figure 1. The unit cell is a simple tetragonal with two copper and two iodine atoms. The coordinates of these atoms with respect to the coordinate system at the point 0 are: (i) $(-a/4, -a/4, -\bar{z}c)$; (ii) $(a/4, -a/4, 0)$; (iii) $(-a/4, a/4, 0)$; (iv) $(a/4, a/4, (\frac{1}{2} - \bar{z})c)$; with $\bar{z} \approx 0.28$ [1]. For $\bar{z} = 0.25$ there is an ideal crystal structure belonging to the space group D_{4h}^7 with 16 symmetry operations. The generating elements [7] of the space group D_{4h}^7 are the operators

$$\{I|000\} \quad \{C_{2x}|\frac{1}{2}a00\} \quad \{C_{4z}^+|\frac{1}{2}a00\}$$

where C_{2x} and C_{4z}^+ are associated with the non-primitive translations. The matrix representatives belonging to the irreducible representations of the small group $G(\mathbf{k})$ for \mathbf{k} at the points and along the symmetry lines in the BZ (figure 2) are given in table 1. The small representations are obtained by Neto's program [8] except for Σ and S directions[†] where the tables from Bradley and Cracknell [7] are used along with necessary modifications due to the different choice of the origin of coordinate system.

The $5s^2p^5$ configuration of I and $3d^{10}4s^1$ configuration of Cu are taken into consideration. Appropriate symmetrised linear combinations of atomic orbitals (SLCAO) are given in table 2. They are obtained on the basis of the procedure described in [9].

3. The Hermitian form of the chemical pseudopotential

Within the framework of the chemical pseudopotential method [5, 6] energy eigenvalues $E(\mathbf{k})$ of the crystal Hamiltonian are obtained by solving the secular equation

$$|A_{ij} - E(\mathbf{k})\delta_{ij}| = 0 \quad (1)$$

[†] There is certain instability in Neto's program when the irreducible representations are calculated along these directions in the BZ. The cause of this instability is not known to us.

Table 1. Matrices of the irreducible representations of the small group $G(k)$ for k at the points and along the symmetry lines in the BZ for the space group D_{4h}^7 . Each representation is completely determined by giving matrices for the generating elements. The matrices for all other elements of a group can be calculated from the given matrices.

(a) $\Gamma(Z)$			
	$\{I 000\}$	$\{C_{2z} \frac{1}{2}a00\}$	$\{C_{4z}^+ \frac{1}{2}a00\}$
1^+	1	1	1
2^+	1	-1	1
3^+	1	1	-1
4^+	1	-1	-1
5^+	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$
1^-	-1	1	1
2^-	-1	-1	1
3^-	-1	1	-1
4^-	-1	-1	-1
5^-	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$
(b) $\Sigma(S)^{a,b}$			
	$\{C_{2z} \frac{1}{2}a\frac{1}{2}a0\}$	$\{\sigma_z \frac{1}{2}a\frac{1}{2}a0\}$	
1	p	p	
2	$-p$	p	
3	p	$-p$	
4	$-p$	$-p$	
(c) $M(A)$			
	$\{\sigma_x \frac{1}{2}a00\}$	$\{C_{2x} \frac{1}{2}a00\}$	$\{C_{4z}^+ \frac{1}{2}a00\}$
1	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
2	$\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$
3	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
4	$\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$
(d) $Y(T)^c$			
	$\{C_{2z} \frac{1}{2}a00\}$	$\{\sigma_y 0\frac{1}{2}a0\}$	
1	$\begin{pmatrix} \beta & 0 \\ 0 & -\beta \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$	
(e) $X(R)$			
	$\{C_{2z} \frac{1}{2}a00\}$	$\{C_{2y} 0\frac{1}{2}a0\}$	$\{\sigma_x \frac{1}{2}a00\}$
1	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
2	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$

(continued overleaf)

Table 1. *continued*

$(f) \Delta(U)^d$		
	$\{C_{2y} 0\frac{1}{2}a0\}$	$\{\sigma_x 0\frac{1}{2}a00\}$
1	β	1
2	β	-1
3	$-\beta$	1
4	$-\beta$	-1
$(g) \Lambda(V)$		
	$\{C_{4z}^+ 0\frac{1}{2}a00\}$	$\{\sigma_y 0\frac{1}{2}a0\}$
1	1	1
2	1	-1
3	-1	1
4	-1	-1
5	$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$
$(h) W$		
	$\{C_{2z} 0\frac{1}{2}a\frac{1}{2}a0\}$	$\{\sigma_y 0\frac{1}{2}a0\}$
1	1	1
2	1	-1
3	-1	1
4	-1	-1

^a [7], p 348.

^b $p = e^{-i\pi l}$, $0 (\Gamma) \leq l \leq 1 (M)$, $(0 (Z) \leq l \leq 1 (A))$.

^c $\beta = e^{-i\pi l/2}$, $0 (X) \leq l \leq 1 (M)$, $(0 (R) \leq l \leq 1 (A))$.

^d $\beta = e^{-i\pi l/2}$, $0 (\Gamma) \leq l \leq 1 (X)$, $(0 (Z) \leq l \leq 1 (K))$.

where A_{ij} is

$$A_{ij} = (\Omega_j/\Omega_i)^{1/2} \sum_{m=1}^N \exp[i\mathbf{k}(\mathbf{R}_m + \boldsymbol{\tau}_\alpha - \boldsymbol{\tau}_\beta)] D_{1j,mi}. \tag{2}$$

Indices i and j in (2) denote type of atoms α and β in the unit cell and their appropriate quantum numbers. \mathbf{R}_m is the lattice vector, $\boldsymbol{\tau}_\alpha$ and $\boldsymbol{\tau}_\beta$ are vectors of non-primitive translations and N is the number of unit cells in the crystal. Ω_j and Ω_i are normalised factors determined on the basis of formula (4) in [10].

$D_{1j,mi}$ is the interaction matrix

$$D_{1j,mi} = \sum_{nl} \left(\sum_{r'i'} (S^{-1})_{1j,r'i'} \langle \phi_{r'i'} | V_{nl}^{mi} | \phi_{mi} \rangle (1 - \delta_{mn} \delta_{il}) - \varepsilon_{mi} \delta_{1m} \delta_{nm} \delta_{li} \delta_{ij} \right) \tag{3}$$

where S^{-1} is the inverse of the overlap matrix. In formula (3) the first sum indices, as well as the first atomic orbital indices $\phi_{r'i'}$, ϕ_{mi} , always correspond to the lattice vectors, whereas the second ones mean the same as i and j in formula (2). V_{nl}^{mi} is equal to

$$V_{nl}^{mi} = V_i(m) - V_i(n) \tag{4}$$

where $V_i(m)$ and $V_i(n)$ are atomic potentials in the unit cells m and n , centred at respective sites. For our calculation two approximations have been used in formula (3):

Table 2. The symmetrised linear combinations of the 5s, 5p (I) and 4s, 3d (Cu) atomic orbitals. Subscripts 1, 2, 3, 4, denote the atoms on which the orbitals are centred (figure 1). $s, x, y, \dots, z^2, x^2 - y^2, xy, \dots$ denote $s, p_x, p_y, \dots, d_{3z^2-r^2}, d_{x^2-y^2}, d_{xy}, \dots$ functions.

(a) $\Gamma(Z)$	
1 ⁺	$s_1 + s_4 (s_1 - is_4), z_2^2 + z_3^2, z_1 - z_4 (z_1 + iz_4), s_2 + s_3$
3 ⁺	$(x^2 - y^2)_2 + (x^2 - y^2)_3$
4 ⁺	$xy_2 + xy_3$
5 ⁺	$\begin{cases} x_1 - x_4, xz_2 + xz_3 \\ y_1 - y_4, yz_2 + yz_3 \end{cases}$
1 ⁻	$xy_2 - xy_3$
2 ⁻	$s_1 - s_4 (s_1 + is_4), (x^2 - y^2)_2 - (x^2 - y^2)_3, z_1 + z_4 (z_1 - iz_4)$
4 ⁻	$s_2 - s_3, z_2^2 - z_3^2$
5 ⁻	$\begin{cases} x_1 + x_4, xz_2 - xz_3 \\ y_1 + y_4, yz_2 - yz_3 \end{cases}$
(b) $\Sigma(S)$	
1	$s_1 + s_4 (s_1 - is_4), s_2 + s_3, z_2^2 + z_3^2, x_1 + y_1 + x_4 + y_4 (x_1 + y_1 - i(x_4 + y_4)),$ $z_1 - z_4(z_1 + iz_4), xy_2 + xy_3, xz_2 - yz_2 - xz_3 + yz_3$
2	$x_1 - y_1 + x_4 - y_4 (x_1 - y_1 - i(x_4 - y_4)), (x^2 - y^2)_2 + (x^2 - y^2)_3,$ $xz_2 + yz_2 - xz_3 - yz_3$
3	$s_2 - s_3, z_2^2 - z_3^2, x_1 - y_1 - x_4 + y_4 (x_1 - y_1 + i(x_4 - y_4)), xy_2 - xy_3,$ $xz_2 - yz_2 + xz_3 - yz_3$
4	$s_1 - s_4 (s_1 + is_4), x_1 + y_1 - x_4 - y_4 (x_1 + y_1 + i(x_4 + y_4)), z_1 + z_4 (z_1 - iz_4),$ $(x^2 - y^2)_2 - (x^2 - y^2)_3, xz_2 + yz_2 + xz_3 + yz_3$
(c) M(A)	
1	$\begin{cases} xz_2 - yz_3 \\ yz_2 - xz_3 \end{cases}$
2	$\begin{cases} x_1 - y_4 (x_1 + iy_4), (x^2 - y^2)_2 \\ y_1 - x_4 (y_1 + ix_4), (x^2 - y^2)_3 \end{cases}$
3	$\begin{cases} s_1, z_1, xz_2 + yz_3 \\ s_4, z_4, yz_2 + xz_3 \end{cases}$
4	$\begin{cases} s_2, z_2^2, x_1 + y_4 (x_1 - iy_4), xy_3 (xy_2) \\ s_3, z_3^2, y_1 + x_4 (y_1 - ix_4), xy_2 (xy_3) \end{cases}$
(d) Y(T)	
1	$\begin{cases} s_1, s_2, z_2^2, x_1, y_4, z_1, (x^2 - y^2)_2, xy_3 (xy_2), xz_2, yz_3 (yz_2) \\ s_4, s_3, z_3^2, x_4, y_1, z_4, (x^2 - y^2)_3, xy_2 (xy_3), xz_3, yz_2 (yz_3) \end{cases}$
(e) X(R)	
1	$\begin{cases} s_1, s_2, z_2^2, y_1, z_1, (x^2 - y^2)_2, yz_2 \\ s_4, s_3, z_3^2, y_4, z_4, (x^2 - y^2)_3, yz_3 \end{cases}$
2	$\begin{cases} x_1, xy_2, xz_2 \\ x_4, xy_3, xz_3 \end{cases}$
(f) $\Delta(U)$	
1	$s_1 + s_4 (s_1 - is_4), s_2 + s_3, z_2^2 + z_3^2, y_1 + y_4 (y_1 - iy_4), z_1 - z_4 (z_1 + iz_4), (x^2 - y^2)_2 + (x^2 - y^2)_3, yz_2 - yz_3$
2	$x_1 - x_4 (x_1 + ix_4), xy_2 - xy_3, xz_2 + xz_3$
3	$s_1 - s_4 (s_1 + is_4), s_2 - s_3, z_2^2 - z_3^2, y_1 - y_4 (y_1 + iy_4), z_1 + z_4 (z_1 - iz_4),$ $(x^2 - y^2)_2 - (x^2 - y^2)_3, yz_2 + yz_3$
4	$x_1 + x_4 (x_1 - ix_4), xy_2 + xy_3, xz_2 - xz_3$

(continued
overleaf)

Table 2. continued

(g) Λ	
1	$s_1, s_4, s_2 + s_3, z_2^2 + z_3^2, z_1, z_4, (x^2 - y^2)_2 - (x^2 - y^2)_3$
2	$xy_2 - xy_3$
3	$s_2 - s_3, z_2^2 - z_3^2, (x^2 - y^2)_2 + (x^2 - y^2)_3$
4	$xy_2 + xy_3$
5	$\begin{cases} x_1, x_4, xz_2, xz_3 \\ y_1, y_4, yz_2, yz_3 \end{cases}$
(h) V	
1	$s_4, z_4, yz_2 + xz_3$
2	$xz_2 - yz_3$
3	$yz_2 - xz_3$
4	$s_1, z_1, xz_2 + yz_3$
5	$\begin{cases} s_2, z_2^2, x_1, x_4, (x^2 - y^2)_2, xy_3 \\ s_3, z_3^2, y_1, y_4, (x^2 - y^2)_3, xy_2 \end{cases}$
(i) W	
1	$s_3, s_4, z_3^2, y_1, z_4, (x^2 - y^2)_3, yz_3$
2	x_1, xy_3, xz_2
3	$s_1, s_2, z_2^2, z_1, y_4, (x^2 - y^2)_2, yz_3$
4	x_4, xy_2, xz_3

the first one is to take into account only terms appropriate to a two-centre approximation, like in a diatomic molecule, while the second consists of assuming the atomic orbitals centred on different sites in a crystal to be approximately orthogonalised.

Thus only two-centre matrix elements appear in the off-diagonal components $D_{1j,mi}$, in the following form:

$$\int_{\Omega_B} \phi_{1j}^*(\mathbf{r}_A) [V_i(m) - V_j(1)] \phi_{mi}(\mathbf{r}_B) d^3r_B. \quad (5)$$

The method for their calculation that we applied in this paper is described in [11, 12], so that only practical calculation details will be presented here. \mathbf{r}_A and \mathbf{r}_B in (5) are the position vectors relative to the two nuclei A and B and Ω_B is an integration sphere centred at B. The radius of the sphere is determined by the point where the two atomic potentials are equal. Integration (5) is reduced to a simple radial integration using the expansion of a spherical harmonic on one site about another and the orthogonality of the spherical harmonics on one site [13]. The radial part of the atomic orbitals used here are the analytic Roothaan–Hartree–Fock functions

$$R_{nl}(r) = \sum_{p=1}^{N_g} c_{nlp} [(2n_{lp})!]^{-1/2} (2\xi_{lp})^{n_{lp}+1/2} r^{n_{lp}-1} e^{-\xi_{lp}r} \quad (6)$$

where the parameters c_{nlp} , n_{lp} , ξ_{lp} and number N_g for each atom are given in [14]. Interactions are considered for inter-atomic distances up to 12 au.

The appropriate atomic eigenvalues ε_i [15] are used as diagonal matrix elements in $D_{1j,mi}$ instead of the values

$$\varepsilon_{mi} = \varepsilon_i + \sum'_{nl} \left(\langle \phi_{mi} | V_{nl}^{mi} | \phi_{mi} \rangle - \sum_{kj} \sum_{rj'} \langle \phi_{mi} | \phi_{kj} \rangle (S^{-1})_{kj,rj'} \langle \phi_{rj'} | V_{nl}^{mi} | \phi_{mi} \rangle \right). \quad (7)$$

The matrix D in (2) is a non-Hermitian matrix [6]. The explicit proof that the energy eigenvalues for non-Hermitian pseudopotential equation are real is given in [16]. Owing to the approximations used in our model this proof cannot be applied, so that the problem of reality of energy will appear. Then the non-Hermitian matrix should be transformed into Hermitian ones [17, 18]. This transformation corresponds to the substitution of the off-diagonal matrix elements $D_{lj,mi}$ and $D_{mi,lj}$ by the mean value

$$D'_{lj,mi} = D'_{mi,lj} = (D_{lj,mi} + D_{mi,lj})/2. \quad (8)$$

The band structure of CuI v calculated in this way is shown in figure 3. The energy gap is 2.21 eV, that is, it is 20% lower than the experimental one. The next level in the conduction band lies very high, at 9.07 eV.

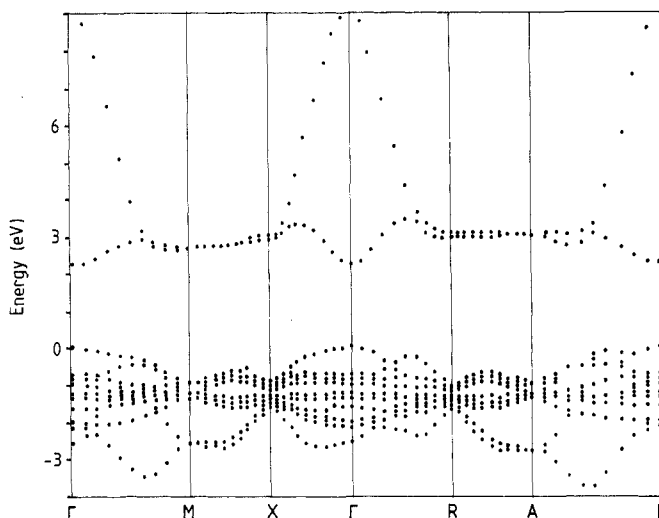


Figure 3. The band structure of CuI v obtained by applying the chemical pseudopotential in Hermitian form (see formula (8)). The lowest 5s states of I are not shown.

A problem appeared while trying to classify wavefunctions according to the irreducible representations of the small group $G(\mathbf{k})$. Therefore the whole calculation procedure is carried out twice for the ideal crystal structure ($\bar{z} = 0.25$): (a) a non-symmetrised basis with 20 orbitals has been used and (b) the SLCAO wavefunctions have been used as basis sets and secular equations of the corresponding order have been solved.

By comparing the results obtained, the following conclusions have been drawn: the same energy levels are obtained only in the case when the corresponding matrix elements $D_{lj,mi}$ and $D_{mi,lj}$ are equal. For instance, the energy levels with Cu atomic orbitals d_{xy} or $d_{x^2-y^2}$ appear in both cases with the same wavefunctions. In all other cases there was a smaller or greater difference between the energy levels calculated using (a) and (b). The most noticeable deviation is in the levels with atomic wavefunctions having magnetic quantum number $m = 0$. Precisely, the problem is caused by p_z orbitals. After averaging (8), the most dominant matrix elements $(s(\text{Cu})p(\text{I}))_\sigma$ appear with the same sign as that of matrix elements $(s(\text{Cu})s(\text{I}))_\sigma$. Therefore at the top of the valence band and next to the s orbitals a combination p_z of the I orbitals forbidden by symmetry appears. It has

been shown that due to the approximation (8) atomic orbitals p_z act as if they have symmetry properties of s orbitals. This does not only happen on the top of the valence band. By calculating the band structure along the direction Δ in the BZ and by checking all the wavefunctions in all the bands, it has been shown that the orbitals p_z always behave in this way; table 2 shows that the following combinations of the atomic s and p_z orbitals correspond to the irreducible representation Δ_1 : $s_1 + s_4$, $s_2 + s_3$ and $p_{z_1} - p_{z_4}$. However, in the cases when the given combination of s orbitals appear, the orbitals p_z appear as $p_{z_1} + p_{z_4}$. This is the characteristic combination for the irreducible representation Δ_3 . The opposite also holds true: along with the allowed combinations of s orbitals of the irreducible representation Δ_3 ($s_1 - s_4$ and $s_2 - s_3$), the orbitals p_z appear as $p_{z_1} - p_{z_4}$, that is, as if they are s orbitals. Otherwise it has not been noticed that the p_z orbitals appear in combinations with other, symmetrically not allowed, atomic orbitals.

4. Non-Hermitian approach

Within this approach the basis set SLCAO orbitals is used separately for each irreducible representation in the secular equation (1). The approximation (8) has not been used. This is an important approach since the matrix D in (2) is known to be non-Hermitian and thus the choice of the basis wavefunctions affects the results obtained for band structure. In this way the possibilities offered by the mathematical apparatus of group theory are most effectively used.

At the Γ point real energy eigenvalues are obtained for all irreducible representations except for Γ_5^+ where an imaginary component forms $\sim 2\%$ of the real part. The results obtained are shown on the left side of figure 4. We can add that in our calculation the $5s$ states of I are treated separately since they are situated ~ 10 eV below the p and d atomic levels and thus form a rather isolated s -like band.

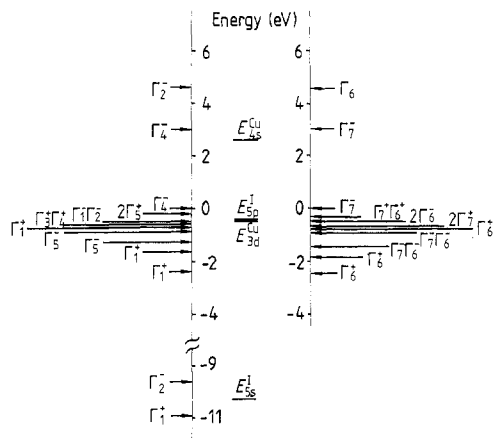


Figure 4. The band structure of CuI v at the Γ point obtained by applying the non-Hermitian chemical pseudopotential. Left side: spin-orbit coupling omitted. Right side: spin-orbit coupling included.

The energy gap is 2.97 eV. The analysis of the results has shown that the energy levels, whose difference defines the energy gap, corresponds to the irreducible representation Γ_4^- with wavefunctions that in general form represent a mixture of $4s$ and $3d$ atomic

wavefunctions of Cu (table 2). The difference between the atomic levels $E_{4s}^{\text{Cu}} - E_{3d}^{\text{Cu}} = 3.18$ eV used in this paper is very close to the experimental value of the energy gap (figure 4), so that the chemical pseudopotential, as a 'weak perturbation', can closely describe the band gap of CuI v. This is further confirmed by the fact that when the 4s level in the calculation is treated separately, that is, when s-d matrix elements are excluded, the calculated value of the energy gap is 2.81 eV. Atomic, non-relativistic sc potentials (and non-relativistic levels) are used here with full Slater exchange ($\alpha = 1$) [15]. The free choice of the parameter α gives semi-empirical character to this calculation.

The lowest conduction band is almost completely derived from 4s Cu levels:

$$\Gamma_4^- \quad \gamma(s_2 - s_3) + \delta(d_{3z^2-r_2^2} - d_{3z^2-r_3^2})$$

where $\gamma^2 + \delta^2 = 1$. The respective coefficient values are $\gamma^2 = 0.99$ and $\delta^2 = 0.01$. According to the data given in [1] the level order at the top of the valence band appears to be

$$E(2\Gamma_5^+) \quad E(\Gamma_4^-) \quad E(2\Gamma_5^-).$$

In our case the level order is the opposite. The wavefunction of the top of the valence band has the same form as in the lowest conduction band, but with coefficients

$$\Gamma_4^- \quad \gamma^2 = 0.06 \quad \delta^2 = 0.94.$$

The level $E(2\Gamma_5^+) = -0.21$ eV (figure 4) lies below $E(\Gamma_4^-)$. The p-d hybridisation is the strongest in the states corresponding to this level:

$$2\Gamma_5^+ \begin{cases} \alpha(p_{x_1} - p_{x_4}) + \beta(d_{xz_2} + d_{xz_3}) \\ \alpha(p_{y_1} - p_{y_4}) + \beta(d_{yz_2} + d_{yz_3}). \end{cases}$$

The admixture coefficients α and β can be used to characterise the strength of p-d hybridisation of the valence band. Our results $\alpha^2 = 0.60$ and $\beta^2 = 0.40$ are in good agreement with the results given in [1] ($\alpha^2 = 0.61$ and $\beta^2 = 0.39$). For the irreducible representation Γ_5^- , two levels are obtained in the states, being obviously of d and p character, respectively:

$$E(\Gamma_5^-) \begin{cases} -0.86 \text{ eV} & (d_{xz_2} - d_{xz_3}) & (d_{yz_2} - d_{yz_3}) \\ -1.27 \text{ eV} & (p_{x_1} + p_{x_4}) & (p_{y_1} + p_{y_4}). \end{cases}$$

The energy difference between the highest valence band and next lowest conduction band is 4.67 eV. This difference is 2.17 eV in [1]. The valence band width is 10.87 eV compared to ~ 7 eV in [1].

In [1] the effect of spin-orbit (so) coupling in the highest valence band at the Γ point of the BZ has been examined and it has been shown that the so splitting is responsible for the difference between the edge excitons in the spectrum (0.465 eV at 6.5 GPa, see figure 6 in [1]). The so interaction effects are also included in this calculation at the Γ point. By the general procedure described in [16], the chemical pseudopotential of the so interaction is derived (see Appendix). For the Γ point the formula is rather simple and it comes to involvement of the atomic data

$$\frac{1}{2}(E_{\text{SO}}^\uparrow + E_{\text{SO}}^\downarrow) \tag{9}$$

in the diagonal matrix elements for p and d states, respectively. The atomic parameter

Table 3. Matrices of the irreducible representations at the Γ point of the BZ for the double space group^a.

	$\{C_{4z}^+ \frac{1}{2}a00\}$	$\{C_{2z} \frac{1}{2}a00\}$	$\{I 000\}$
6^+	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
7^+	$\frac{1}{\sqrt{2}}\begin{pmatrix} -1 & 1 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
6^-	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
7^-	$\frac{1}{\sqrt{2}}\begin{pmatrix} -1 & 1 \\ -1 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
	$\{\bar{C}_{4z}^+ \frac{1}{2}a00\}$	$\{\bar{C}_{2z} \frac{1}{2}a00\}$	$\{\bar{I} 000\}$
6^+	$\frac{1}{\sqrt{2}}\begin{pmatrix} -1 & -1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
7^+	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$
6^-	$\frac{1}{\sqrt{2}}\begin{pmatrix} -1 & -1 \\ 1 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$
7^-	$\frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

^a [7], p 523.

of the so interaction for Cu ($\xi_{\text{Cu}} = 4.6 \times 10^{-3}$) is obtained by means of the Wood–Boring program [19] whereas for I it is obtained by means of interpolation on the basis of the data presented in [15] ($\xi_{\text{I}} = 2.6 \times 10^{-2}$).

The irreducible representation matrices appropriate for the double space group for the elements of the group generators are taken from Bradley and Cracknell [7] (table 3). The symmetrised combination of atomic wavefunctions with spinors is shown in table 4.

Table 4. The symmetrised linear combinations of atomic orbitals with spinors (u_-, u_+) at the Γ point, where

$$\begin{aligned}
 F &= x_1 - x_4 + i(y_1 - y_4) & P &= xz_2 - xz_3 + i(yz_2 - yz_3) \\
 G &= xz_2 + xz_3 + i(yz_2 + yz_3) & f &= (x^2 - y^2). \\
 R &= x_1 + x_4 + i(y_1 + y_4)
 \end{aligned}$$

6^+	$ \begin{cases} Fu_- + F^*u_-, Gu_- + G^*u_+, (z_1 - z_4)(u_- - u_+), (z_2^2 + z_3^2)(u_- - u_+), \\ (s_2 + s_3)(u_- - u_+) \\ Fu_+ - F^*u_+, Gu_+ - G^*u_+, (z_1 - z_4)(u_- + u_+), (z_2^2 + z_3^2)(u_- + u_+), \\ (s_2 + s_3)(u_- + u_+) \end{cases} $
7^+	$ \begin{cases} F^*u_- + Fu_+, G^*u_- + Gu_+, (f_2 + f_3)(u_- - u_+), (xy_2 + xy_3)(u_- + u_+) \\ F^*u_+ - Fu_+, G^*u_+ - Gu_+, (f_2 + f_3)(u_- + u_+), (xy_2 + xy_3)(u_- - u_+) \end{cases} $
6^-	$ \begin{cases} Ru_- - R^*u_-, P^*u_- - Pu_+, (z_1 + z_4)(u_- + u_+), (xy_2 - xy_3)(u_- + u_+) \\ Ru_+ + R^*u_+, P^*u_+ + Pu_+, (z_1 + z_4)(u_- - u_+), (xy_2 - xy_3)(u_- - u_+) \end{cases} $
7^-	$ \begin{cases} R^*u_- - Ru_+, Pu_- + P^*u_+, (z_2^2 - z_3^2)(u_- + u_+), (s_2 - s_3)(u_- + u_+), \\ (f_2 + f_3)(u_- + u_-) \\ R^*u_+ + Ru_+, Pu_+ + P^*u_+, (z_2^2 - z_3^2)(u_- - u_+), (s_2 - s_3)(u_- - u_+), \\ (f_2 - f_3)(u_- - u_+) \end{cases} $

The calculation shows that there are no changes in the level order at the top of the valence band (figure 4). The difference of the appropriate levels is

$$E(\Gamma_7^-) - E(\Gamma_7^+, \Gamma_6^+) = 0.3 \text{ eV}$$

$$E(\Gamma_7^-) - E(2\Gamma_6^-) = 0.45 \text{ eV}.$$

On the basis of these results we cannot with assurance confirm that within our approach the SO coupling on the top of the valence band is responsible for the appearance of the absorption peaks in figure 6 in [1].

The calculation of the band structure in other directions and at other points in the BZ has not given the expected results. This mostly refers to the band structure along the directions Δ and Σ in the BZ, where the two bands intersect the band gap, and this has been checked by appropriate analytical calculations. This situation has not been essentially changed by involving the 5s wavefunctions of I in the basis set.

5. Conclusions

It has been shown in this paper that by using the chemical pseudopotential in the Hermitian form, that is, by using the approximation (8), the band structure of CuI *v* can be calculated. The results for the energy gap are in a better agreement with the experimental ones than those obtained by the previous LMTO method. The disadvantage of this method is in the fact that most of the wavefunctions cannot be classified according to the irreducible representations of the small group $G(\mathbf{k})$. This is a consequence of the approximation (8) by which, for instance, the symmetry of the atomic orbital p_z has been changed. This essentially affects the shape of the band structure.

The non-Hermitian chemical pseudopotential with SLCAO basis sets provides accurate calculation of the energy gap only at the Γ point of the BZ. The failure of the attempt to calculate the full band structure reveals a much deeper disagreement between the mathematical apparatus of group theory and our model of the non-Hermitian chemical pseudopotential.

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Appendix. The chemical pseudopotential of the spin-orbit interaction: derivation for the Γ point of the BZ

Starting from Weisz's assumption [20] that the part of the Hamiltonian corresponding to the SO interaction term can be expressed in the form of a sum of isolated atomic so

contributions

$$H^{\text{SO}} = \sum_i H_i^{\text{SO}} \quad (\text{A1})$$

the chemical pseudopotential [16] with so interaction included can be written in the form

$$\left[T + V_m + H_m^{\text{SO}} + \sum_{n \neq m} (V_n^m + H_n^{m\text{SO}}) - P^{\mathcal{D}}(V_n^m + H_n^{m\text{SO}}) \right] |\phi_{mi}^{\mathcal{D}}\rangle = \varepsilon_{mi}^{\mathcal{D}} |\phi_{mi}^{\mathcal{D}}\rangle. \quad (\text{A2})$$

Equation (A2) is analogous to equation (15) in [16]. $\phi_{mi}^{\mathcal{D}}$ in (A2) is a SLCAO function with basis spinors (u_+ , u_-) and \mathcal{D} denotes the corresponding irreducible representation of the double space group (table 3).

By applying the procedure described in [16] and the approximations from § 3, the interaction matrix is obtained in the following form:

$$D_{ki',mi}^{\mathcal{D}} = \sum_n [\langle \phi_{ki'}^{\mathcal{D}} | V_n^m + H_n^{m\text{SO}} | \phi_{mi}^{\mathcal{D}} \rangle (1 - \delta_{mn}) + \varepsilon_{mi}^{\mathcal{D}} \delta_{km} \delta_{ii'} \delta_{nm}]. \quad (\text{A3})$$

The secular equation matrix elements are related to the interaction matrix similarly as in formula (2):

$$A_{ij}^{\mathcal{D}} = \sum_m \exp(i\mathbf{k}\mathbf{R}_m) D_{1j,mi}^{\mathcal{D}} \quad (\text{A4})$$

that is,

$$A_{ij}^{\mathcal{D}} = \varepsilon_{ii}^{\mathcal{D}} \delta_{ij} + \sum_m' \exp(i\mathbf{k}\mathbf{R}_m) \langle \phi_{1j}^{\mathcal{D}} | V_1^m | \phi_{mi}^{\mathcal{D}} \rangle + \sum_m' \exp(i\mathbf{k}\mathbf{R}_m) \langle \phi_{1j}^{\mathcal{D}} | H_1^{m\text{SO}} | \phi_{mi}^{\mathcal{D}} \rangle \quad (\text{A5})$$

while only two-centre matrix elements from (A3) are taken into consideration here. The last term in (A5) is eliminated when the band structure is calculated at the Γ point since

$$H^{\text{SO}} = \frac{\hbar^2}{4m^2c^2} \frac{1}{r} \frac{dV}{dr} \mathbf{r} \times \mathbf{k} \cdot \boldsymbol{\sigma}. \quad (\text{A6})$$

For $\varepsilon_{ii}^{\mathcal{D}}$ in (A5) an approximate formula is

$$\varepsilon_{ii}^{\mathcal{D}} \approx \langle \phi_{ii}^{\mathcal{D}} | H_a | \phi_{ii}^{\mathcal{D}} \rangle \quad (\text{A7})$$

where H_a is a Hamiltonian of the isolated atom with so term included.

Thus the secular equation matrix elements at the Γ point are finally calculated according to the following formula:

$$A_{ij}^{\mathcal{D}} = \langle \phi_{ii}^{\mathcal{D}} | H_a | \phi_{ii}^{\mathcal{D}} \rangle \delta_{ij} + \sum_m' \langle \phi_{1j}^{\mathcal{D}} | V_1^m | \phi_{mi}^{\mathcal{D}} \rangle. \quad (\text{A8})$$

By concrete calculation of the diagonal matrix elements for the irreducible representation given in table 3 and by using the SLCAO functions with spinors in table 4, formula (9) in this paper can be proved.

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