

Jacek C. Wojdeł · Stefan T. Bromley

From cluster calculations to molecular materials: a mixed pseudopotential approach to modeling mixed-valence systems

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Abstract In this paper we present a technique for finding an appropriate parameterization of ultrasoft pseudopotentials for modeling mixed-valence materials. For the example of hexacyanometallate molecular building blocks, we show how ionic cluster calculations can be used to determine a set of parameters for the metal centers. Pseudopotentials chosen in such a way are then shown to be suitable for periodic calculations of the corresponding mixed-valence materials (e.g., Prussian Blue).

Keywords Prussian blue · Mixed-valence materials · DFT · Ultrasoft pseudopotentials

Introduction

Mixed-valence materials [1] are of particular interest for fundamental research and applications because of their complex magnetic, electronic, and optical properties. One of the prototypical examples of such materials is Prussian Blue (PB), which forms the basis for a rich family of structural derivatives [2]. The basic building block of PB analogues is the hexacyanometallate complex (i.e. a metal ion center surrounded by six cyanide

ligands) arranged in a face centered cubic lattice (see Fig. 1). There are two primary types of sites in this lattice: a strong crystal-field site coordinated to the carbon side of the ligand, and a weak crystal-field site coordinated to the nitrogen side of the ligand. Additionally, the interstitial cations located within the cubic lattice give the unit cell charge neutrality. The number and charge of these cations depends strongly on the oxidation level of the metal centers that form the iron-cyanide lattice.

In the case of PB, the material is built of Fe^{2+} and Fe^{3+} centers, making it a typical example of a class II mixed-valence material [1]. The additional, interstitial cations are usually alkaline metals (from Na^+ to Cs^+), but other metals have also been reported in literature [3], along with the introduction of water-filled vacancies [2]. Depending on the exact crystal structure, PB has been reported to form crystals with lattice constants ranging from 10.11 to 10.20 Å [4–8]. Recently, many PB analogues have been shown to exhibit interesting magnetic [9–11], optical [12], and electrochemical [13, 14] properties, which have been utilized in numerous different applications [4, 10, 15, 16].

The two closest derivatives to PB are Prussian Yellow (PY) and Everitt's Salt (ES). These two compounds can be obtained from PB by electrochemical oxidation and reduction, respectively [17]. The resulting structures contain only Fe^{3+} centers in case of PY, or only Fe^{2+} centers in case of ES. Although these materials are therefore no longer of mixed-valence nature, they share many of the mixed-valence characteristics. The two different types of sites in the crystal lattice can still be distinguished by the strength of the crystal field in which they reside. In the resulting structure, the carbon-coordinated sites contain low spin iron centers, while the nitrogen-coordinated ones contain high-spin iron centers.

Modeling materials that contain different oxidation levels or different electronic states for the same atomic species is a challenging task. Subtle differences in the electronic structure of the species in question at different sites within the material need to be described accurately

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J. C. Wojdeł (✉)
Ceramic Membrane Centre “The Pore”, DelftChemTech,
Delft University of Technology, Julianalaan 136,
2628 BL, Delft, The Netherlands
E-mail: J.C.Wojdel@tnw.tudelft.nl
Tel.: +31-15-278-9418
Fax: +31-15-278-4289

S. T. Bromley
Dept. Química Física and Centre Especial de
Recerca en Química Teòrica, Universitat de
Barcelona and Parc Científic, c/Marti i Franques 1,
E-08028 Barcelona, Spain
E-mail: S.Bromley@qf.ub.es

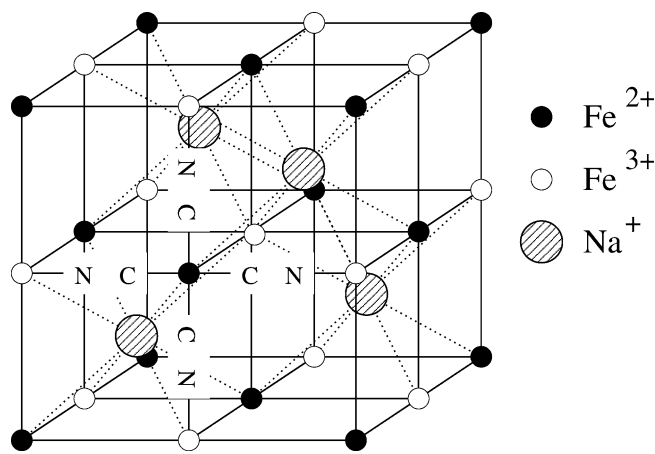


Fig. 1 Structure of densely packed Prussian blue with no vacancies— $\text{NaFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$

in the simulation environment. In all ab initio calculations one needs to choose the approximations carefully in order to find a proper balance between accuracy and computational cost. The planewave pseudopotential (PW-PP) approach to solving the Kohn–Sham density functional (DF) equations for periodic solids is one example of such a balance in action. In PW-PP calculations the core regions of the atoms within the solid are represented by a non-physically smooth wavefunction, which results from parameterized atomic PPs. This property is especially evident when using Vanderbilt’s ultrasoft pseudopotentials (USPPs) [18]. The use of USPPs allows for relatively low kinetic energy cut-offs, making the calculations much more efficient than with the more traditional norm-conserving PPs. It is also commonly argued that USPPs are more transferable between different electronic states than norm-conserving PPs [19].

In our recent work [20], we have shown that it is not simply possible to model PB and related systems using a uniform USPP for both (carbon- and nitrogen-coordinated) types of metal sites. We proposed there a novel approach of mixing different parameterizations of USPPs depending on the coordination of the site. In this paper we present a technique for choosing the appropriate parameterization based on small calculations of ionic metal-cyanide clusters, and show that the resulting USPPs can be transferred to fully periodic calculations of real materials.

Computational methods

All calculations were performed using the PP-PW method for solving the Kohn–Sham equations using the Perdew and Wang-generalized gradient approximation (PW91) functional [21]. For cluster calculations we used the CPMD code (version 3.7.2) [22]. For the fully periodic calculations we used the Dacapo code, version 2.7.4, from the Campos Atomistic Simulation

Environment [23]. The use of two different PP-PW codes was required due to the fact that of the two, only CPMD allows for modeling charged molecules, while only Dacapo allows sampling of k -points.

In the calculations we used USPPs that were generated using version 7.3.4 of the Vanderbilt’s USPP generation code [24]. In the presented study, all of the supporting species (nitrogen, carbon, and sodium) are modeled using standard USPPs obtained from the Vanderbilt library. For the iron centers we use three differently parameterized USPPs:

P-I The original USPP from the Vanderbilt library, parameterized on the basis of a neutral iron atom. The reference electronic configuration for this USPP is $3d^6 4s^1 4p^1$. It is parameterized with 3 β -functions and an Ar core.

P-II USPP parameterized on the $3d^6 4s^2$ reference configuration. It is parameterized with 6 β -functions and a Ne core.

P-III USPP parameterized to fit the $3d^5$ (+3 cation) configuration of iron. It is parameterized with 5 β -functions and a Ne core.

For ionic cluster calculations, we center the molecule in a 15 Å box. The molecule is then relaxed to obtain the equilibrium geometry. The kinetic energy cutoff is set to about 400 eV, and the calculations are done in a spin-polarized regime. In order to scan a suitable range of the ionic configurations, we calculated structures of the following model systems:

$\text{Fe}(\text{CN})_6^{3-}$ - corresponding to the low spin Fe^{III} site in PY,

$\text{Fe}(\text{CN})_6^{4-}$ - corresponding to the low spin Fe^{II} site in PB and ES,

$\text{Fe}(\text{NC})_6^{3-}$ - a system with the cyanide ligands rotated so that they point with the nitrogen end to the iron center, corresponding to the high spin Fe^{III} site in PB and PY.

The symmetry of the molecules was fixed to $m3m$ and remained enforced during the calculations.

All of the periodic calculations were done in spin-polarized regime with no constraints on the magnetic moment of the unit cell. We chose to do the calculations with a relatively high kinetic energy cutoff of 600 eV. At this cutoff, the energetics of the unit cell are fully converged. In order to improve the stability of the calculations we used a finite electronic temperature of 0.2 eV, which results in a slight smearing of electrons around the Fermi level.

In order to calculate the structural properties of the materials, we performed a potential energy surface (PES) scan by varying the lattice constant. The ionic relaxation was done using $2 \times 2 \times 2$ Monkhorst–Pack set of k -points [25]. After scanning a suitable range of lattice constants, the lattice constant with minimal energy was obtained from a quadratic fit to the calculated points on the PES. To refine the accuracy of the calculated atomic

Table 1 Calculated geometries of different iron cyanide ionic clusters (all values in angstroms). Experimental mean values and standard deviations are reported in the last row

	$\text{Fe}(\text{CN})_6^{3-}$		$\text{Fe}(\text{CN})_6^{4-}$		$\text{Fe}(\text{NC})_6^{3-}$	
	Fe–C	C–N	Fe–C	C–N	Fe–N	C–N
P-I	2.292	1.191	2.604	1.192	2.467	1.194
P-II	1.897	1.191	1.891	1.193	1.871	1.195
P-III	2.046	1.187	2.047	1.187	2.009	1.196
<i>Exp.</i>	1.93 ± 0.03	1.16 ± 0.04	1.93 ± 0.07	1.16 ± 0.04	2.10 ± 0.07	1.16 ± 0.02

positions, in the previously optimized unit cell, we performed further structural relaxation calculations using a higher number of k -points. For the structural relaxations within the equilibrium unit cell we chose a $4 \times 4 \times 4$ Monkhorst–Pack set of k -points, which is reduced by the symmetry of the unit cell to ten independent k -points.

Results

Cluster calculations

Table 1 summarizes the calculated geometries of the ionic clusters. As can be seen, the geometries of the clusters studied vary widely depending on the choice of iron USPP. In order to compare these values with the experimentally available data, we scanned the Inorganic Crystal Structure Database [26], and selected 58 structures containing iron coordinated to six cyanide ligands. The average Fe–C distance in those structures is 1.93 Å, the average Fe–N distance is 2.10 Å, and the average C–N distance is 1.16 Å. The collected average geometrical properties divided between appropriate oxidation states of iron centers are shown at the bottom of Table 1. In our calculations, the C–N distance is systematically overestimated for all clusters studied (Appendix). This can be explained easily by the fact that the clusters are studied in gas phase, giving the outermost atoms freedom to expand.

More important is the strong dependency of the resulting geometries on the choice of USPP. Clearly, the P-I USPP is not suitable for modeling iron in cyanide complexes, as it overestimates the metal–ligand distances by almost 0.5 Å (this USPP performs very well for bulk iron, according to the results available from the CAM-POS website). For the other two USPPs, one can see that P-II gives geometries that agree with the experimental Fe–C distance within 0.05 Å margins, while P-III geometries agree with the experimental Fe–N distance up to 0.1 Å. The choice of the appropriate USPP for the different sites in PB is therefore straightforward: P-II for the carbon-coordinated low spin site, P-III for the nitrogen-coordinated high spin site.

Periodic calculations

Having chosen the appropriate USPPs for different metal sites in PB and its closest analogues, we can

proceed to fully periodic calculations of these materials. Table 2 summarizes the resulting geometrical properties of all materials modeled. As can be seen, the lattice constants obtained lay well within the range of the reported experimental values. The structural differences between the oxidized and reduced forms of PB are small, in line with the small calculated differences between $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ clusters. Because PB is an ill-defined system in experiments, the reported range of measured lattice constants is larger than our calculated difference between studied materials. As expected, the C–N distance is slightly shortened with respect to the ionic cluster calculations; however, it still overestimates the experimental value by about 0.03 Å. The crystal structures obtained retain $m\bar{3}m$ symmetry of the primary PB lattice to within 0.01 Å. The interstitial Na^+ cations are located centrally in the cubes formed by iron centers.

The high accuracy of the calculated geometries is expected because the USPPs were chosen specifically on the basis of the ionic cluster geometries obtained. One needs to check therefore, whether the modeled structures also exhibit appropriate electronic properties. Table 2 summarizes the calculated electronic properties of PY, PB, and ES. In accordance with the model proposed by Xidis and Neff [17], PB itself is an intrinsic semiconductor (although with an underestimated band-gap, as usual in DF-calculations). At the same time its reduced and oxidized forms are calculated to be electron- and hole-conductors, respectively. The calculated magnetic moments of PB and ES are as expected for each of these compounds (see Table 3). Interestingly, in the case of PY, the average 4.3 unpaired electrons per $\text{Fe}^{\text{HS}}-\text{Fe}^{\text{LS}}$ pair show some interaction between electrons residing on different iron centers. This superexchange type of interaction, facilitated by the antibonding π^* orbital of the cyanide ligand, is in accordance with the earlier theoretical investigations [2].

Table 2 Calculated geometries of Prussian blue and related materials (all values in angstroms)

	Prussian yellow	Prussian blue	Everitt's salt
a	10.13	10.16	10.19
a_{exp}	10.20^{a}	$10.11-10.20^{\text{b}}$	
$Fe-C$	1.88	1.87	1.90
$C-N$	1.18	1.18	1.18
$N-Fe$	2.00	2.02	2.02

^a Ref. [11].

^b Refs. [4–8].

Table 3 Electronic properties of Prussian blue and related materials. Magnetic moment is given in Bohr-magnetrons per Fe^{HS} – Fe^{LS} pair

	Prussian yellow	Prussian blue	Everitt's salt
Conductivity type	Hole conductor	Semiconductor	Electron conductor
Magnetic moment	4.31	5.00	4.03

Summary and conclusions

In this paper we have presented a technique for using small cluster calculations as guidance for the choice of appropriate parameterizations of USPPs to be used in

fully periodic calculations of molecular mixed valence materials. Given a number of different USPPs parameterized with different levels of approximation and based on different reference states, one can compare the calculated geometries of small clusters to the reference measurements, and based on that comparison, select the best USPP for each crystal environment.

The strength of the technique lies in the fact that once the appropriate choice has been made, the USPPs can be used throughout a range of different materials (given that they share the appropriate crystal environments). The calculated structures obtained are both geometrically and electronically valid.

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Appendix

Table 4 List of experimental structures used for comparison with cluster calculations

Compound	Authors	Year
Cs ₂ Li(Fe(CN) ₆)	Beall GW, Milligan WO, Korp J, Bernal I, McMullan R	1977
Fe ₄ (Fe(CN) ₆) ₃ (H ₂ O) ₁₄	Buser HJ, Schwarzenbach D, Petter W, Ludi A	1977
LaKFe(CN) ₆ (H ₂ O) ₄	Beall GW, Mullica DF, Milligan WO	1978
LaFe(CN) ₆ (H ₂ O) ₅	Bailey WE, Williams RJ, Milligan WO	1973
H ₃ Fe(CN) ₆	Haser R, de Broin CE, Pierrot M	1972
Na _{0.672} Ni _{4.8} (Fe(CN) ₆) _{2.6}	Zilberman MV, Kuznetsova VG, Volkhin VV	1974
Cs ₂ MgFe(CN) ₆	Swanson BI, Hamburg SI, Ryan RR	1974
K ₂ Zn ₃ (Fe(CN) ₆) ₂ (H ₂ O) ₅	Gravereau P, Garnier E, Hardy AM	1979
Cs ₂ LiFe(CN) ₆	Swanson BI, Ryan R	1973
Na ₃ Fe(CN) ₆ (H ₂ O) ₂	Katila T, Leskelae M, Niinistoe L, Riski KJ, Valkonen J, Ylae-Jaeaeski J	1980
K ₄ Fe(CN) ₆ (H ₂ O) ₃	Kiryama R, Kiriyama H, Wada T, Niizeki N, Hirabayashi H	1964
Cs ₂ KFe(CN) ₆	Herren F, Ludi A	1979
La(Fe(CN) ₆) ₆ (H ₂ O) ₄	Mullica DF, Milligan WO, Garner RL	1980
La(Fe(CN) ₆) ₆ (H ₂ O) ₅	Mullica DF, Milligan WO, Garner RL	1980
Cs ₂ ZnFe(CN) ₆	Kuznetsov VG, Maksimova SI	1973
K ₃ Fe(CN) ₆	Vannerberg NG	1972
Fe ₄ (Fe(CN) ₆) ₃ (H _{0.67} D _{.33}) ₂ O) ₁₄	Herren F, Fischer P, Ludi A, Haelg W	1980
Cs ₂ ZnFe(CN) ₆	Kuznetsov VG, Popova SV, Seifer GB	1970
K ₄ Fe(CN) ₆ (D ₂ O) ₃	Taylor JC, Mueller MH, Hitterman RL	1970
Cu ₂ Fe(CN) ₆	Rigamonti R	1937
K ₂ CuFe(CN) ₆	Rigamonti R	1937
K ₂ Cu ₃ (Fe(CN) ₆) ₂	Rigamonti R	1937
Li ₂ CuFe(CN) ₆	Rigamonti R	1937
Na ₂ CuFe(CN) ₆	Rigamonti R	1937
(NH ₄) ₂ CuFe(CN) ₆	Rigamonti R	1937
Rb ₂ CuFe(CN) ₆	Rigamonti R	1937
K ₂ NiFe(CN) ₆	Rigamonti R	1938
Ni ₂ Fe(CN) ₆	Rigamonti R	1938
K ₂ CoFe(CN) ₆	Rigamonti R	1938
Co ₂ Fe(CN) ₆	Rigamonti R	1938
H ₄ (Fe(CN) ₆)	Pierrot M, Kern R, Weiss R	1966
(Zn ₃ (Fe(CN) ₆) ₂) _{1.3333} (H ₂ O) _{19.22}	Gravereau P, Garnier E	1984
K ₃ Fe(CN) ₆	Figgis BN, Gerloch M, Mason R	1969
K ₃ Fe(CN) ₆	Figgis BN, Gerloch M, Mason R	1969
N(CH ₃) ₄ MnFe(CN) ₆ (H ₂ O) ₈	Babel D, Kurtz W	1983
Cs ₂ Na(Fe(CN) ₆)	Fletcher SR, Gibb TC	1977
Cs ₂ K(Fe(CN) ₆)	Fletcher SR, Gibb TC	1977
K ₃ (Fe(CN) ₆)	Figgis BN, Skelton BW, White AH	1978
K ₃ (Fe(CN) ₆)	Figgis BN, Skelton BW, White AH	1978
CeK(Fe(CN) ₆) ₆ (H ₂ O) ₄	Mullica DF, Milligan WO, Oliver JD	1979
Na _{0.95} Cu _{3.52} (Fe(CN) ₆) ₂	Bennett BA, Shahbandeh MR, Streat M	1982
K ₃ (Fe(CN) ₆)	Morioka Y, Toriumi K, Ito T, Saito A, Nakagawa I	1985
K ₃ (Fe(CN) ₆)	Morioka Y, Toriumi K, Ito T, Saito A, Nakagawa I	1985

Table 4 (Contd.)

Compound	Authors	Year
Cs ₂ LiFe(CN) ₆	Chadwick BM, Jones DW, Wilde HJ, Yerkess J	1985
PrKFe(CN) ₆ (H ₂ O) ₄	Mullica DF, Sappenfield EL, Perkins HO	1988
Bi(Fe(CN) ₆ (H ₂ O) ₄	Mullica DF, Perkins HO, Sappenfield EL	1988
PrKFe(CN) ₆ (H ₂ O) ₄	Mullica DF, Sappenfield EL, Perkins HO	1988
(Ag(NH ₃) ₂)Ag ₂ (Fe(CN) ₆)	Ziegler B, Seitz K, Babel D	1988
SmFe(CN) ₆ (H ₂ O) ₄	Mullica DF, Perkins HO, Sappenfield EL, Grossie DA	1988
Sm(Fe(CN) ₆ (H ₂ O) ₄	Mullica DF, Sappenfield EL	1989
ErFe(CN) ₆ (H ₂ O) ₄	Gramlich V, Petter W	1990
Sm(Fe(CN) ₆ (H ₂ O) ₄	Petter W, Gramlich V, Hulliger F	1988
ErFe(CN) ₆ (H ₂ O) ₄	Dommann A, Vetsch H, Hulliger F, Petter W	1990
Bi(Fe(CN) ₆ (H ₂ O) ₄	Petter W, Gramlich V, Dommann A, Vetsch H, Hulliger F	1990
Fe ₄ (Fe(CN) ₆) ₃	Herren F, Fischer P, Ludi A, Haelg W	1980
Fe ₄ (Fe(CN) ₆) ₃ ((H _{0.67} D _{0.33}) ₂ O) ₁₄	Herren F, Fischer P, Ludi A, Haelg W	1980
Fe(Fe(CN) ₅ (NO))(H ₂ O) ₃	Mullica DF, Tippin DB, Sappenfield EL	1991
Fe ₄ ((Re(CN) ₆ Se ₈) ₃ (H ₂ O) ₃₆	Bennett MV, Beauvais LG, Shores MP, Long JR	1901

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