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Hardness conservation as a new transferability criterion: application to fully non-local pseudopotentials

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Abstract

The concept of chemical hardness has been recently adopted in the framework of Kohn-Sham theory as a faithful *ab initio* measure of pseudopotential transferability. A fully self-consistent hardness theory has been developed and employed to evaluate the transferability of semilocal pseudopotentials. Hardness contains most of the relevant physical information determining the transferability of pseudopotentials, and is an important step forward with respect to the logarithmic derivatives analysis. We discuss the main features of chemical hardness, and the relations between chemical hardness and the original definitions of absolute and local hardness. We then apply the new criterion to investigate the transferability of fully non-local Kleinman-Bylander pseudopotentials. Hardness conservation allows us to obtain a meaningful comparison between them and the conventional norm-conserving ones and give us a criterion to improve the pseudopotential tranferability of fully non-local pseudopotentials by suitably resetting their local part.

77.80.Bh, 61.50.Lt, 64.60.Cn, 64.70.-p

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I. INTRODUCTION

In the framework of density-functional theory and the pseudopotential approximation, many efforts have been made to find physical properties able to predict *a priori* (i.e. just in the atomic reference configuration) the degree of transferability of pseudopotentials. Logarithmic derivative analysis has shown to be an important tool to test pseudopotential transferability, but not a sufficient criterion of transferability for all atoms of the periodic table. The chemical hardness defined in the context of Janak theory has been proposed[1] as an optimum physical quantity to test pseudopotentials for all atoms. The fully self-consistent hardness has been calculated[2] and employed to study transferability of HSC-type semilocal pseudopotentials.

In this work we focus on the relations between hardness and other two important quantity in the physics of electronic systems, the absolute hardness,[3] and the local hardness.[4,5] Then, we employ the hardness conservation criterion to test the transferability of norm-conserving pseudopotentials arranged in the fully non-local structure.[14]

II. THEORY

A. Absolute and local hardness

Chemical hardness, along with the chemical potential, is one of the most important quantities determining the physics of many-electron systems. *Absolute hardness* was introduced by Parr and Pearsons[3] as,

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_v = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_v \tag{1}$$

where E, N, μ and v denote total energy, number of particles, chemical potential and external potential of the many electron system, respectively.

A local expression for the hardness has been introduced in the framework of DFT,[4,5]

$$\eta(\mathbf{r}) = \frac{1}{2N}\int d\mathbf{r}' \frac{\delta^2 F}{\delta\rho(\mathbf{r})\,\delta\rho(\mathbf{r}')}\,\rho(\mathbf{r}')\,, \tag{2}$$

with

$$F[\rho] = E[\rho] - \int d\mathbf{r}\, v(\mathbf{r})\, \rho(\mathbf{r}) \tag{3}$$

It has been shown[5] that

$$\eta = \int d\mathbf{r}\, \eta(\mathbf{r})\, \tilde{f}(\mathbf{r}) \tag{4}$$

where $\tilde{f}$ is the Fukui function,

$$\tilde{f}(\mathbf{r}) = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_v = \left[\frac{\partial \mu}{\partial v(\mathbf{r})}\right]_N \tag{5}$$

Local hardness and Fukui function are key quantities to investigate the reactivity of atomic and molecular systems.[6–9]

B. Hardness for fractional occupation numbers

In the framework of Janak theory, Teter[1] defined the chemical hardness to be the matrix

$$H_{ij} = \frac{1}{2}\frac{\partial^2 E[\rho]}{\partial f_i \partial f_j} = \frac{1}{2}\frac{\partial \epsilon_i}{\partial f_j} \tag{6}$$

where E is the Janak functional[10] and f_i the occupation number of the ith state. Thus, the hardness matrix measures the first-order change of an energy eigenvalue resulting from a variation of an occupation number, while allowing the total number of electrons to vary. The idea of Teter was to employ the hardness matrix in the pseudopotential theory as a measure of transferability. Due to the big amount of physical information contained in the hardness, a comparison between its atomic all-electron and pseudo values realizes a meaningful test of transferability.

Here we give only a very short description of formulation that has been developed to calculate in practice H_{ij}. All the details and the comments about the physical contents of hardness can be found in Ref. 2.

The atomic hardness in non-relativistic non-spin polarized formulation is given by,

$$H_{\substack{nlm \\ n'l'm'}} = \frac{1}{2} \int \int d\mathbf{r}\, d\mathbf{r}'\, n_{nlm}(\mathbf{r})\, w_{\text{hxc}}(\mathbf{r}, \mathbf{r}')\, \frac{\delta \rho(\mathbf{r}')}{\delta f_{n'l'm'}} \ . \tag{7}$$

where,

$$n_{nlm}(\mathbf{r}) = R^2_{nl}(r)\, |Y_{lm}(\Omega)|^2 \ , \tag{8}$$

$$w_{\text{hxc}}(\mathbf{r}, \mathbf{r}') = \frac{\partial V_{\text{hxc}}(\mathbf{r})}{\partial \rho(\mathbf{r}')} \ , \tag{9}$$

$$\rho(\mathbf{r}) = \sum_{nlm}^{\text{occ}} f_{nlm}\, n_{nlm}(\mathbf{r}) \ . \tag{10}$$

The density change due to the variation of occupation numbers consists of two terms:

$$\frac{\delta \rho(\mathbf{r})}{\delta f_{nlm}} = n_{nlm}(\mathbf{r}) + \Delta n_{nlm}(\mathbf{r}) \ . \tag{11}$$

The first term arises from the explicit dependence of density on the occupation numbers, while the second involves relaxation of the wavefunction with changes of occupation. We will refer to the neglect of Δn_{nlm} as the “frozen wavefunction approximation” (FWA), while the effect of the Δn_{nlm} term will be referred to as the “self-consistency” (SC) correction. By defining

$$V_{nlm}(\mathbf{r}) = \int d\mathbf{r}'\, w_{\text{hxc}}(\mathbf{r}, \mathbf{r}')\, n_{nlm}(\mathbf{r}') \ . \tag{12}$$

We obtain the following expression for the hardness:

$$H_{\substack{nlm \\ n'l'm'}} = \frac{1}{2} \int d\mathbf{r}\, V_{nlm}(\mathbf{r})\, n_{n'l'm'}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r}\, V_{nlm}(\mathbf{r})\, \Delta n_{n'l'm'}(\mathbf{r}) \tag{13}$$

The first term is the FWA hardness and it can be easily calculated. The second is the SC correction and can be calculated to linear order in perturbation theory by considering V_{nlm} as a bare potential perturbation and $\Delta n_{n'l'm'}$ the self-consistent change of the charge density due to the perturbation,

$$\Delta n_{nlm}(\mathbf{r}) = \int d\mathbf{r}'\, \chi(\mathbf{r}, \mathbf{r}')\, V_{nlm}(\mathbf{r}') \tag{14}$$

where χ is the linear susceptibility. The determination of the linear susceptibility follows closely the modified Sternheimer approach discussed by Mahan and Subbaswamy.[11,12]

C. Relations between chemical and absolute hardness

In this section we focus on the relations between the matrix elements of the fractional occupation hardness and both absolute and local hardness.

We start considering a system with a zero-temperature Fermi-Dirac distribution of occupation numbers. For atomic and molecular systems, the Fukui function and the chemical potential are discontinuous functionals of N for any integer value. Also, for insulators, a discontinuity arises at the gap. At $T = 0$, the Fukui function can be immediately related to the charge density change given by Eq.(11).

The left derivative (i.e., derivative from below) of the charge density with respect to N ($\delta N = \delta f_{\rm homo}$, where HOMO stands for the Highest Occupied Molecular Orbital) is given by

$$\tilde{f}^{-}(\mathbf{r}) = |\psi_{\rm homo}(\mathbf{r})|^2 \, + \, \sum_{i}^{1,M} f_i \, \frac{\delta |\psi_i(\mathbf{r})|^2}{\delta f_{\rm homo}}, \tag{15}$$

where M is the number of occupied states, $f_i = 1$ for $i = 1, M-1$ and $f_i = f_{\rm homo}$ for $i = M$. The right derivative ($\delta N = \delta f_{\rm lumo}$, where LUMO stands for Lowest Unoccupied Molecular Orbital) is,

$$\tilde{f}^{+}(\mathbf{r}) = |\psi_{\rm lumo}(\mathbf{r})|^2 \, + \, \sum_{i}^{1,M} f_i \, \frac{\delta |\psi_i(\mathbf{r})|^2}{\delta f_{\rm lumo}} \tag{16}$$

where $f_i = 1$ for $i = 1, M$.

Perdew *et al.*[13] proved the equalities $\mu^+ = \epsilon_{\rm lumo}$ and $\mu^- = \epsilon_{\rm homo}$, where μ^+ and μ^- are the right and left derivatives of the energy with respect to N. The chemical potential is defined as $\mu = 1/2(\epsilon_{\rm homo} + \epsilon_{\rm lumo})$. Obviously, the absolute hardness is discontinuous for integer N:

$$\eta^- \; = \; \frac{1}{2}\left(\frac{\delta \epsilon_{\rm homo}}{\delta f_{\rm homo}}\right) \tag{17}$$

$$\eta^+ \; = \; \frac{1}{2}\left(\frac{\delta \epsilon_{\rm lumo}}{\delta f_{\rm lumo}}\right) \tag{18}$$

so we take $\eta = \frac{1}{2}\left(\eta^{+} + \eta^{-}\right)$, where

$$\eta^{-} = \frac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}'\, n_{\mathrm{homo}}(\mathbf{r})\, w_{\mathrm{hxc}}(\mathbf{r},\mathbf{r}')\, \frac{\delta\rho(\mathbf{r}')}{\delta f_{\mathrm{homo}}}\ . \tag{19}$$

$$\eta^{+} = \frac{1}{2}\int\int d\mathbf{r}\, d\mathbf{r}'\, n_{\mathrm{lumo}}(\mathbf{r})\, w_{\mathrm{hxc}}(\mathbf{r},\mathbf{r}')\, \frac{\delta\rho(\mathbf{r}')}{\delta f_{\mathrm{lumo}}}\ . \tag{20}$$

where $n_{homo(lumo)} = |\psi_{homo(lumo)}|^2$. Thus, we have related the absolute hardnesses η^{-} and η^{+} back to the diagonal elements $H_{\mathrm{homo,homo}}$ and $H_{\mathrm{lumo,lumo}}$ of the hardness matrix, respectively. Also, taking

$$\eta^{\pm} = \int d\mathbf{r}\, \tilde{f}^{\pm}(\mathbf{r})\, \eta^{\pm}(\mathbf{r}) \tag{21}$$

from Eq. (18) and (19) we obtain an expression for the local hardness,

$$\eta^{-}(\mathbf{r}) \ = \ \int d\mathbf{r}'\, w_{\mathrm{hxc}}(\mathbf{r},\mathbf{r}')\, n_{\mathrm{homo}}(\mathbf{r}') \tag{22}$$

$$\eta^{+}(\mathbf{r}) \ = \ \int d\mathbf{r}'\, w_{\mathrm{hxc}}(\mathbf{r},\mathbf{r}')\, n_{\mathrm{lumo}}(\mathbf{r}') \tag{23}$$

It should be noted that calculation of $\tilde{f}^{+}$, η^{+} and $\eta^{+}(\mathbf{r})$ of atoms and molecules will be strongly affected by LDA error.

For a metallic system there is no discontinuity in the chemical potential. The various HOMO- and LUMO-related quantities coincide and all the previous expressions involving left and right limits simplify to just one.

It is an artifact of the LDA that for many open-shell systems, the ground state has degenerate eigenvalues with fractional occupation numbers. In such a case, a relation between the change of electron number and the occupation of eigenstates is difficult to obtain. The added fraction of electron number will be redistributed among one-electron states to minimize the total energy, and we can argue δN should be a linear combination of δf for all fractionally occupied states, the weights being generally hard to predict.

For open-shell atoms, the fractional occupations of the degenerate HOMOs are typically equal, so that the spherical symmetry of the potential is preserved. In such a case, the occupation numbers are simply linearly related to the electron number, and there are no discontinuities. Letting l be the angular momentum of the HOMO (suppressing the n index and spin), the Fukui function is given by

$$\tilde{f} = \frac{1}{2l+1} \sum_{m}^{-l,+l} \frac{\delta \rho}{\delta f_{lm}} \tag{24}$$

having taken

$$\frac{\delta f_{lm}}{\delta N} = \frac{1}{2l+1} \; . \tag{25}$$

Thus we have

$$\eta = \frac{1}{2} \frac{1}{2l+1} \sum_{m'}^{-l,+l} \frac{\delta \epsilon_{lm}}{\delta f_{lm'}} \; . \tag{26}$$

Then, from Eq. (24) we obtain,

$$\eta = \frac{1}{2} \int\int d\mathbf{r}\, d\mathbf{r}'\, n_{lm}(\mathbf{r})\, w_{\mathrm{hxc}}(\mathbf{r},\mathbf{r}')\, \tilde{f}(\mathbf{r}') \; . \tag{27}$$

It should be noted that η in Eq. (27) does not really depend on m, because the Fukui function has spherical symmetry. The above formulation can easily be extended to closed-shell atoms, for which the discontinuities will clearly reappear.

In Table 1 we showed the absolute hardness values for some atoms calculated by means of Eq.(26), and compared with experimental values[3] calculated in according to the finite difference expression $\eta^{exp} = (1/2)(I - A)$, being I and A the ionization potential and the electronic affinity, respectively. For the open-shell atoms (C,O and Si) the agreement is very good. For Ti^{2+} η is computed as the average between its left and right values. In such a case the deviation from the experimental value is reasonable at all, because for closed-shell atoms the difference between HOMO and LUMO eigenvalues contributes to the finite-difference expression of hardness as well.

D. Hardness generalization to non-diagonal occupation numbers

The hardness matrix has been further generalized to non diagonal occupation numbers.[2] This extension allows one to consider the change of occupation with respect to any specified angular component of the density. In a perturbation theory framework, the density of the perturbed system in terms of the eigenstates of the unperturbed one will be,

$$n(\mathbf{r}) = \sum_{ij} f_{ij}\, \psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) \tag{28}$$

Instead of working in the explicit atomic representation $f_{ij} = f_{nlm,n'l'm'}$, we find it convenient to work in a representation $(nn'll'LM)$ in which LM are labels of total angular momentum, and $L = |l-l'|, |l-l'|+2, ..., l+l'$ following the usual angular-momentum addition rules. Introducing the index $\alpha = nn'll'$, we thus have

$$n(\mathbf{r}) = \sum_{\alpha LM} f_{\alpha LM}\, n_\alpha(r)\, Y_{LM}(\Omega) \tag{29}$$

where $n_\alpha = R_{nl}\, R_{n'l'}$ and

$$f_{\alpha LM} = \sum_{mm'} C(LM; lm, l'm) f_{nlm,n'l'm'} \tag{30}$$

The $C(LM; lm, l'm)$ are Clebsch-Gordon coefficients. The generalized Kohn-Sham eigenvalues are given by

$$\epsilon_{\alpha LM} = \frac{\partial E}{\partial f_{\alpha LM}}\ , \tag{31}$$

and the generalized hardness matrix, because of the radial symmetry of unperturbed configuration, is

$$H_{\alpha\beta LL'MM'} = \frac{1}{2}\frac{\partial^2 E}{\partial f_{\alpha LM}\, \partial f_{\beta L'M'}} = H_{\alpha\beta L}\, \delta_{LL'}\delta_{M,-M'}\ . \tag{32}$$

where

$$H_{\alpha\beta L} = \frac{1}{2}\int\int dr\, dr'\ r^2\, r'^2\, n_\alpha(r)\, w_{\rm hxc}^{(L)}(r,r')\, \frac{\delta\rho(r')}{\delta f_\beta}\ . \tag{33}$$

As in the diagonal case, the density variation due to the change of occupation numbers consists of the FWA contribution and the SC one. Calculation of $H_{\alpha\beta L}$ has been performed with the same procedure used before for the diagonal case.[2]

III. RESULTS

Hardness conservation can be considered as an important step forward with respect to the logarithmic derivative criterion. It contains all the most important “first principles” properties needed to characterize pseudopotential transferability. It gives information about changes of both the electrostatic and exchange-correlation part of pseudopotential with respect to occupation number changes of any angular character.

Moreover, the fully self consistent hardness takes into account wavefunction relaxations caused by charge rearrangement. This feature gives us a sound guide to analyze pseudopotential transferability. Analysis of the hardness matrix enables us not only to carry out meaningful transferability tests in a large ensemble of physical environments, but also to detect what kind of atomic characteristic can damage the transferability of pseudopotentials. Also, it inserts norm-conservation and the Louie-Froyen-Cohen correction in a more rigorous theoretical framework. Hardness is a linear-order property. Its range of accuracy might be be insufficient to test pseudopotential features involving large deviation from the atomic reference configuration. For instance, considering fully non-local pseudopotentials, hardness is generally insensitive to the presence of possible ghost states below the reference atomic eigenvalue. In fact, wavefunction relaxation needed to pinpoint a ghost level[16] can't be achieved by means of a linear-order approximation. Nonetheless, many atomic species show a quite extended linearity interval around eigenvalues, and in those cases, hardness is meaningful and accurate. Detailed hardness analysis characteristics for a set of representative atoms with HSC-type pseudopotentials[15] can be found in Ref. 2. In what follows, we present a hardness comparison between semilocal HSC and fully non local KB[14] pseudopotentials employing the non-diagonal hardness formulation. To this end, its useful to consider the *average hardness error*.[2] This quantity consists of a weighted average of hardness matrix elements that represent at best the typical changes occurring in the occupation numbers when we pass from reference to hybridized configurations. In such a way, the large amount of physical information of the whole matrix is compressed into a single number.

The average hardness error X is defined as

$$X^2 \;=\; \sum_{\alpha\beta L} w_{\alpha\beta L}\,(\Delta H_{\alpha\beta L})^2\;. \tag{34}$$

ΔH is the difference between all-electron and pseudopotential hardness matrix elements, and $w_{\alpha\beta L}$ is a weight. Thus, X is just a weighted RMS average of the errors in the hardness matrix elements. The weights are taken to be

$$w_{\alpha\beta L} \;=\; (2L+1)\,\eta_{l_\alpha}\,\eta_{l'_\alpha}\,\eta_{l_\beta}\,\eta_{l'_\beta}\;, \tag{35}$$

and

$$\eta_l \;=\; (2l+1)\,\sqrt{2f_l(1-f_l)} \tag{36}$$

We refer the reader to Ref. 2 for the discussion of this choice. It's clear from Eq. (35) that X tends to weight more shells which are partially occupied than empty or fully occupied ones.

In general, the fully non-local modification of semilocal pseudopotentials should produce an overall deterioration of its transferability. KB-like pseudopotentials are constructed as to be equal to semilocals in the reference atomic configuration. Such a correspondence is lost once we movie out of that. Thus, the FWA hardness of semilocal and KB potentials will be the same, but the SC part will not. The arbitrariness contained in the choice of local part of KB potentials should be employed to optimize at best the transferability. In practice this is taken to be equal to the non-local component of pseudopotentials allowing us to get rid of ghost states. Actually, the guideline to reduce both the loss of transferability and the risk to get ghost states is to choose the local part so as to minimize as much as possible the non-local contributions. Optimization of the local part by means of a hardness criterion satisfies this request.

Here, we parameterize the local part of the KB pseudopotentials as a linear combination of the l-dependent radial potentials for s, p, and d

$$V^{KB}_{loc} = \alpha\, V_s + \beta\, V_p + \gamma\, V_d\;. \tag{37}$$

and determine the coefficients α, β, and γ in order to minimize the average hardness error (under the constraint $\alpha + \beta + \gamma = 1$ to ensure the correct behavior of the pseudopotential tail). The hardness error is monitored as function of pseudopotential core radii to focus on the loss of transferability occurring when we enlarge them.

We present results for Ti, Rh and Ge. The first two are characterized (as are most of the transition metals) by strong pseudopotential non-locality. Obviously these are the most interesting cases to investigate (the more the pseudopotential is local, the less important is the choice of local part).

In Figs. 1 and 2, the average errors for Ti are shown. $\langle R_c \rangle$ is the average value of the three core radii R_s, R_p and R_d. We varied $\langle R_c \rangle$ equally enlarging R_s and R_p while R_d has been taken fixed (being the d wavefunction without nodes). In Fig. 1 we see the configuration $(\alpha, \beta, \gamma) = (0, 0, 1)$ (i.e. $V_{loc} = V_d$) gives an error close to that of the semilocal pseudopotential for close $\langle R_c \rangle$.

Configurations $(1, 0, 0)$ and $(0, 1, 0)$ strongly worsen the error. In Fig. 2 we see that a nearly equally weighted mixture of pseudopotentials $(0.3, 0.3, 0.4)$ doesn't give good results, while a combination of the d component with a small fraction of p improves significantly the behavior of the $(0, 0, 1)$ arrangement.

In Fig. 3 we compare for rhodium semilocal and KB pseudopotentials with local part $(0, 1, 0)$, $(0, 0, 1)$ and $(0.8, 0.1, 0.1)$. The first two give small errors, but the third configuration makes the KB errors almost indistinguishable from the semilocal one. Here change of $\langle R_c \rangle$ is obtained by varying all the core radii.

Finally, results for germanium are showed in Fig. 4. Non-locality is weaker here than in the two first cases. We found configurations $(0, 1, 0)$ and $(0.2, 0.4, 0.4)$ are the best suited to fit with semilocal error.

Unfortunately, we do not have any rigorous argument nor a practical recipe to predict the best configuration of the local part. We have to employ qualitative considerations about localization of pseudopotentials, and then to try a good guess. Nonetheless, a few trials are usually sufficient to find mixed configurations giving KB pseudopotentials with improved transferability.

Of course, the (α, β, γ) configurations found for the three atoms treated here are not necessarily optimal, and with further adjustments the errors could probably be further reduced.

IV. CONCLUSION

In this work we presented a theoretical analysis of the connection between our hardness matrix and the absolute hardness.

Also we showed an application of the hardness-conservation criterion to compare the transferability of semilocal and KB pseudopotentials. As could be expected, use of the KB form produces a general decrease of transferability, which however can be strongly limited by a proper choice of local part. We showed that the parameterization of the local part in terms of non-local components gives us a sufficient variational freedom to generate KB pseudopotentials with high transferability as measured by hardness conservation.

TABLES

TABLE I. Table1: calculated absolute hardness values (in Rydberg units) compared with the experimental ones for open- and closed-shell atoms. In cases where the discontinuity doesn't occur, the agreement is quite good

atom	η^{exp}	η	η^{+}	η^{-}
C	0.3674	0.3644		
O	0.4470	0.4953		
Si	0.2484	0.2477		
$Ti^{2+}(4s^2,3d^0)$	0.5144	0.4439	0.5984	0.2894

FIGURES

FIG. 1. Average hardness errors of semilocal and relative KB pseudopotentials arranged with different local parts as functions of the core radii average $\langle R_C \rangle$. Numbers in the legend correspond to the parameters α, β, γ. Taking the d component as local part of KB pseudopotential makes its average error very close to that of the semilocal one for small $\langle R_C \rangle$.

FIG. 2. The choice of a suitable mixed configuration for the local part of KB pseudopotential consistently improves the transferability with respect to take the d component of semilocal as local part.

FIG. 3. The configuration (0.8,0.1,0.1) makes the error for KB pseudopotential almost indistinguishable with respect to that of the semilocal one.

FIG. 4. The two local parts considereds both make the KB pseudopotential in optimum agreement with the semilocal one.

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