CrossMark

REGULAR ARTICLE

The HSAB principle from a finite-temperature grand-canonical perspective

Ramón Alain Miranda-Quintana[1] · Taewon David Kim[1] · Carlos Cárdenas[2,3] · Paul W. Ayers[1]

Abstract We provide a new proof for Pearson's hard/soft acid/base (HSAB) principle. Unlike alternative proofs, we do not presuppose a simplified parabolic dependence on the energy of the system with respect to changes in its number of electrons. Instead, we use the more physically grounded finite-temperature formulation of the grand-canonical ensemble. We show that under the usual assumptions regarding the chemical potentials and hardnesses of the involved species, the HSAB rule holds for a wide range of temperatures.

Keywords Conceptual DFT · Hard/soft acid/base principle · Finite-temperature · Grand-canonical ensemble

1 Introduction

The hard/soft acid/base (HSAB) principle, as it was originally established by Pearson, affirms that *all other things being equal, hard acids prefer binding to hard bases and soft acids prefer binding to soft bases* [1]. Here, *other things* recall that the HSAB is a tie-breaker rule because determining the direction of reactions between acids and bases, the tendency for strong acids to displace weak acids and strong

✉ Ramón Alain Miranda-Quintana
  ramirandaq@gmail.com

[1] Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON, Canada

[2] Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile

[3] Centro para el desarrollo de la Nanociencias y Nanotecnología, CEDENNA, Av. Ecuador 3493 Santiago, Chile

bases to displace weak bases is more dominant. However, if the acids and bases involved in the reaction have similar strengths, then the chemical driving force for the reaction of acids and bases is the relative hardness, hence the HSAB rule [1–3].

In the past, several formal proofs of Pearson's hard/soft acid/base (HSAB) rule [4–11] have been put forward within conceptual density functional theory (c-DFT) [12–23]. (This has also allowed to establish the relation between the HSAB and other reactivity principles.) [9, 24–27]. Almost a decade ago, one of us showed that if the strength of acids and bases could be identified with the (negative) chemical potential, then it is possible to cast a simple, yet incredibly general, proof of the HSAB rule [4]. This proof shows that a double-exchange reaction between hard and soft acids and bases of equal strength is always exothermic if the hard acids in the product are associated with hard bases and soft acids to soft bases. In other words, the equilibrium in the reaction shown below is displaced toward the formation of the products.

$$A_\text{h}B_\text{s} + A_\text{s}B_\text{h} = A_\text{h}B_\text{h} + A_\text{s}B_\text{s} \tag{1}$$
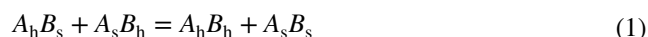
This proof (and also others based on the c-DFT machinery) relies heavily on the precise definition of reactivity descriptors like the chemical potential, μ [28], and chemical hardness, η [29–31]. In c-DFT, the standard approach to define such descriptors is to consider them as derivatives of the ground state energy, E, with respect to the number of electrons, N, namely:

$$\mu = \frac{\partial E}{\partial N} \tag{2}$$

$$\eta = \frac{\partial^2 E}{\partial N^2} \tag{3}$$

This requires working with a model for the variation of E versus N, which considers the energy of systems with non-integer numbers of electrons [32, 33]. This has motivated several models that interpolate the energy between states with integer numbers of electrons [34–36]. However, not all of these models can be supported on physical grounds [37, 38], and some of them could even be internally inconsistent [39]. Another standard approach, working with the zero-temperature formulation of the grand-canonical (GC) ensemble, is also not free of controversy. In this case, the exact E versus N behavior is given by the linear interpolation of Perdew et al. [40–45]. Since this model is not differentiable with respect to the number of electrons when N is an integer, and the higher order side-derivatives are zero, μ and η are ill-defined.

One way around these problems is to work with a finite-temperature formulation of the GC ensemble [46–58]. If the system of interest is in contact with a bath at $T > 0$, the energy (and other state functions) becomes a differentiable function of N, and all the reactivity descriptors are well defined. Our goal in the present work is to analyze the validity of the HSAB rule in the finite-temperature conceptual DFT formalism. This will closely follow the spirit of previous works devoted to the proof of the maximum hardness [59] and the minimum electrophilicity [56] principles.

2 Finite-temperature grand-canonical study of the HSAB principle

When considering nonzero temperatures, the state function that determines the spontaneity of a process is no longer the electronic energy, E, but the electronic Helmholtz free energy, $\mathcal{A}$ [12]

$$\mathcal{A} = E - TS \tag{4}$$

where S is the (electronic) entropy,

$$S = -k_B \text{Tr}(D \ln D) \tag{5}$$

In this expression, D is the density matrix (DM) of the state under analysis, k_B is the Boltzmann constant, and Tr represents the trace of the operator/matrix.

Minimizing $\mathcal{A}$ subject to the constraint that the number of electrons is held constant gives the expression for the equilibrium DM:

$$D = \frac{\exp\left[-\beta\left(\hat{H} - \mu\hat{N}\right)\right]}{\text{Tr}\left\{\exp\left[-\beta\left(\hat{H} - \mu\hat{N}\right)\right]\right\}}; \quad \beta = \frac{1}{k_B T} \tag{6}$$

From here, we can easily see that:

$$\mathcal{A} = \mu N - \frac{1}{\beta}\ln\text{Tr}\left\{\exp\left[-\beta\left(\hat{H} - \mu\hat{N}\right)\right]\right\} \tag{7}$$

Working with $\mathcal{A}$ slightly changes the definitions of the chemical potential and chemical hardness [52]

$$\mu = \frac{\partial\mathcal{A}}{\partial N} = -\frac{I + A}{2} \tag{8}$$

$$\eta = \frac{\partial^2\mathcal{A}}{\partial N^2} = \frac{1 + 2\exp\left(-\beta\frac{\eta_P}{2}\right)}{2\exp\left(-\beta\frac{\eta_P}{2}\right)} \tag{9}$$

$\eta_P = I - A$ is what Malek and Balawender called the Pearson hardness [57], the subindex T in η_T indicates that this is the "thermodynamic chemical hardnesses," and I and A are the ionization energy and electron affinity, respectively. Notice that the second expressions appearing in Eqs. (8) and (9) have been obtained under the assumption that only three states (e.g., with $M, M \pm 1$ electrons) are used to expand the trace appearing in Eq. (7) [49]. While the form of the chemical potential obtained in this way is identical to the standard working expression used in c-DFT, this is not the case for the hardness. This highlights that, in general, using three states to interpolate $\mathcal{A}$ does not give the same results as using the same three states to estimate the trace in Eq. (7) [55]. Nonetheless, in this case, the different hardness expressions are consistent with each other in the sense that their thermodynamic hardness is a monotonic function of the Pearson hardness

$$\eta_{T(X)} > \eta_{T(Y)} \Leftrightarrow \eta_{P(X)} > \eta_{P(Y)} \tag{10}$$

The proof given in Ref. [4] can now be rephrased in terms of the thermodynamic chemical potential and hardness of Eqs. (8) and (9). This will only require another assumption, namely, that we can effectively express the variation of $\mathcal{A}$ with respect to changes in N as:

$$\Delta\mathcal{A} = \frac{\partial\mathcal{A}}{\partial N}\Delta N + \frac{1}{2}\frac{\partial^2\mathcal{A}}{\partial N^2}\Delta N^2 \tag{11}$$

Even though this is a valid procedure, we would like to present an alternative take on the HSAB principle, with more emphasis on the GC formalism, and that does not rely on the truncation of the Taylor expansion of $\mathcal{A}$.

The starting point will be the reaction given in Eq. (1). To proceed, we need to make some assumptions regarding the chemical potentials and harnesses of the species involved in this reaction. For example, we will assume that the chemical potential (strength) of all the acids (bases) is the same [4, 5, 8, 9]:

$$\mu_{A_h} = \mu_{A_s} = \mu_A < \mu_{B_h} = \mu_{B_s} = \mu_B. \tag{12}$$

This corresponds to previously mentioned *all other things being equal* condition imposed by Pearson.

In the case of the hardness, recent arguments in favor of the HSAB principle only require that the hard species are in fact harder than the soft ones [5, 8, 25]. However, these studies are based on a simple parabolic model of the energy

with respect to the number of electrons. Here, we will be working with a more realistic (and, therefore, more difficult to manipulate) model. For this reason, we need to impose an extra condition on the hardnesses, which has been also introduced in previous HSAB proofs [4]:

$$\eta_{A_s} = \eta_{B_s} = \eta_s < \eta_{B_h} = \eta_{A_h} = \eta_h. \tag{13}$$

Proving the HSAB principle is equivalent to show that the variation of the Helmholtz free energy along the reaction, $\Delta\mathcal{A}_{rn}$, is negative:

$$\Delta\mathcal{A}_{rn} = \mathcal{A}_{A_h B_h} + \mathcal{A}_{A_s B_s} - \mathcal{A}_{A_s B_h} - \mathcal{A}_{A_h B_s} < 0 \tag{14}$$

As it is customary, we rewrite $\Delta\mathcal{A}_{rn}$ as:

$$\Delta\mathcal{A}_{rn} = \Delta\mathcal{A}_{A_h B_h} + \Delta\mathcal{A}_{A_s B_s} - \Delta\mathcal{A}_{A_s B_h} - \Delta\mathcal{A}_{A_h B_s} \tag{15}$$

where

$$\Delta\mathcal{A}_{XY} = \mathcal{A}_{X(XY)} + \mathcal{A}_{Y(XY)} - \mathcal{A}_X - \mathcal{A}_Y. \tag{16}$$

Here, $\mathcal{A}_X$ denotes the Helmholtz free energy of the isolated reagent X, and $\mathcal{A}_{X(XY)}$ denotes the Helmholtz free energy of the reagent X when it is placed in a bath whose electron chemical potential is the same as that of molecule XY. In this way, we are assuming that the electron-transfer effects are dominating the reactivity, with negligible contributions from electrostatic, steric, polarization, local, etc., effects.

Given the form of Eq. (7), it is more convenient to work with the auxiliary function $\exp\left(-\beta\Delta\mathcal{A}_{rn}\right)$, so the HSAB rule will be valid if:

$$\exp\left(-\beta\Delta\mathcal{A}_{rn}\right) > 1. \tag{17}$$

Considering again only states with $M_X - 1$, M_X, and $M_X + 1$ electrons when estimating the traces, we have that

$$\exp\left(-\beta\mathcal{A}_X\right) = \exp\left(-\beta E_X^{M_X}\right)\left\{1 + \exp\left[\beta\left(A_X + \mu_X\right)\right] \right.$$
$$\left. + \exp\left[-\beta\left(I_X + \mu_X\right)\right]\right\} \tag{18}$$

$$\exp\left(-\beta\mathcal{A}_{X(XY)}\right) = \exp\left(-\beta E_X^{M_X}\right)\exp\left[-\beta\mu_{XY}\left(N_X - M_X\right)\right]$$
$$\times \left\{1 + \exp\left[\beta\left(A_X + \mu_{XY}\right)\right] + \exp\left[-\beta\left(I_X + \mu_{XY}\right)\right]\right\} \tag{19}$$

with analogous expressions holding for $\exp\left(-\beta\mathcal{A}_Y\right)$ and $\exp\left(-\beta\mathcal{A}_{Y(XY)}\right)$.

It is now easy to see that:

$$\exp\left(-\beta\Delta\mathcal{A}_{XY}\right) = Q_{1XY}Q_{2XY} \tag{20}$$

$$Q_{1XY} = \exp\left[\beta\mu_{XY}\left(N_X - M_X + N_Y - M_Y\right)\right] \tag{21}$$

$$Q_{2XY} = \left\{\frac{1 + \exp\left[\beta\left(A_X + \mu_{XY}\right)\right] + \exp\left[-\beta\left(I_X + \mu_{XY}\right)\right]}{1 + \exp\left[\beta\left(A_X + \mu_X\right)\right] + \exp\left[-\beta\left(I_X + \mu_X\right)\right]}\right\}$$
$$\times \left\{\frac{1 + \exp\left[\beta\left(A_Y + \mu_{XY}\right)\right] + \exp\left[-\beta\left(I_Y + \mu_{XY}\right)\right]}{1 + \exp\left[\beta\left(A_Y + \mu_X\right)\right] + \exp\left[-\beta\left(I_Y + \mu_X\right)\right]}\right\} \tag{22}$$

Here, μ_X indicates the chemical potential of species X when it has M_X electrons (see Eq. 1). The chemical potential of the product, μ_{XY}, can be calculated by the condition that the number of electrons remains constant along the reaction. If we determine the average number of electrons in a reactant as:

$$N_X = M_X + \frac{\exp\left[\beta\left(A_X + \mu\right)\right] - \exp\left[-\beta\left(I_X + \mu\right)\right]}{1 + \exp\left[-\beta\left(I_X + \mu\right)\right] + \exp\left[\beta\left(A_X + \mu\right)\right]} \tag{23}$$

the chemical potential of XY must satisfy the following equation:

$$N_X + N_Y = M_X + M_Y \tag{24}$$

However, from this condition, it is easy to see that:

$$Q_{1XY} = 1 \tag{25}$$

Equation (23) is equivalent to:

$$\exp\left[\beta\left(A_X + \mu_{XY}\right)\right] + \exp\left[\beta\left(A_Y + \mu_{XY}\right)\right]$$
$$- \exp\left[-\beta\left(I_X + \mu_{XY}\right)\right] - \exp\left[-\beta\left(I_Y + \mu_{XY}\right)\right] \tag{26}$$
$$+ 2\exp\left[\beta\left(A_X + A_Y + 2\mu_{XY}\right)\right] - 2\exp\left[-\beta\left(I_X + I_Y + 2\mu_{XY}\right)\right] = 0$$

It is, however, more convenient to rewrite this equation using the auxiliary variables $\Delta\mu_X$ and $\Delta\mu_Y$, defined as:

$$\mu_{XY} = \mu_X + \Delta\mu_X = \mu_Y + \Delta\mu_Y \tag{27}$$

Then, Eq. (26) reads:

$$\exp\left(-\beta\frac{\eta_X}{2}\right)\left[\exp\left(\beta\Delta\mu_X\right) - \exp\left(-\beta\Delta\mu_X\right)\right]$$
$$+ \exp\left(-\beta\frac{\eta_Y}{2}\right)\left[\exp\left(\beta\Delta\mu_Y\right) - \exp\left(-\beta\Delta\mu_Y\right)\right]$$
$$+ 2\exp\left[-\beta\left(\frac{\eta_X + \eta_Y}{2}\right)\right]\left\{\exp\left[\beta\left(\Delta\mu_X + \Delta\mu_Y\right)\right]\right. \tag{28}$$
$$\left. - \exp\left[-\beta\left(\Delta\mu_X + \Delta\mu_Y\right)\right]\right\} = 0$$

where, for notational simplicity, we have dropped the subindex P to refer to the Pearson hardness. Using these variables, Eq. (22) can be rewritten as:

$$Q_{2XY} = \left[\frac{1 + \exp\left(-\beta\frac{\eta_X}{2}\right)\left[\exp\left(\beta\Delta\mu_X\right) + \exp\left(-\beta\Delta\mu_X\right)\right]}{1 + 2\exp\left(-\beta\frac{\eta_X}{2}\right)}\right]$$
$$\times \left[\frac{1 + \exp\left(-\beta\frac{\eta_Y}{2}\right)\left[\exp\left(\beta\Delta\mu_Y\right) + \exp\left(-\beta\Delta\mu_Y\right)\right]}{1 + 2\exp\left(-\beta\frac{\eta_Y}{2}\right)}\right] \tag{29}$$

Combining Eqs. (14)–(22) and (29), we can see that proving the HSAB rule is equivalent to showing that:

$$Q_2 = \frac{q_{hh}q_{ss}}{q_{hs}q_{sh}} > 1 \tag{30}$$

where

$$q_{\sigma\sigma'} = \left[1 + \exp\left(-\beta\frac{\eta_\sigma}{2}\right)\left[\exp\left(\beta\Delta\mu_{A_\sigma}^{\sigma\sigma'}\right) + \exp\left(-\beta\Delta\mu_{A_\sigma}^{\sigma\sigma'}\right)\right]\right]$$
$$\times \left[1 + \exp\left(-\beta\frac{\eta_{\sigma'}}{2}\right)\left[\exp\left(\beta\Delta\mu_{B_{\sigma'}}^{\sigma\sigma'}\right) + \exp\left(-\beta\Delta\mu_{B_{\sigma'}}^{\sigma\sigma'}\right)\right]\right] \tag{31}$$

and

$$\Delta\mu_{X_\sigma}^{\sigma\sigma'} = \mu_{X_\sigma Y_{\sigma'}} - \mu_{X_\sigma}. \tag{32}$$

In principle, we know all the parameters entering Eq. (30), except for the $\Delta\mu_{X_\sigma}^{\sigma\sigma'}$ variables, to which now we turn our attention. It is easy to see that if X and Y have the same hardness (as it is the case in compounds A_hB_h and A_sB_s), then $\Delta\mu_{Y_\sigma}^{\sigma\sigma} = -\Delta\mu_{X_\sigma}^{\sigma\sigma}$ will be a solution to Eq. (28). Thus, following Eq. (27):

$$\Delta\mu_{X_\sigma}^{\sigma\sigma} = \frac{\mu_{Y_\sigma} - \mu_{X_\sigma}}{2} \tag{33}$$

But from Eq. (12):

$$\Delta\mu_{A_h}^{hh} = \Delta\mu_{A_s}^{ss} = -\Delta\mu_{B_h}^{hh} = -\Delta\mu_{B_s}^{ss} = \frac{\mu_B - \mu_A}{2} \equiv r \tag{34}$$

Then, the numerator of Eq. (30) simplifies to:

$$q_{hh}q_{ss} = \left\{ \begin{array}{c} \left[1 + \exp\left(-\beta\frac{\eta_h}{2}\right)\left[\exp(\beta r) + \exp(-\beta r)\right]\right] \times \\ \left[1 + \exp\left(-\beta\frac{\eta_s}{2}\right)\left[\exp(\beta r) + \exp(-\beta r)\right]\right] \end{array} \right\}^2 \tag{35}$$

If we now consider the reagents in Eq. (1) (e.g., species with mixed hardnesses), we can see that if $\Delta\mu_X = x$ and $\Delta\mu_Y = -y$ are solutions to Eq. (28) with hardnesses $\eta_X = a$ and $\eta_Y = b$, then $\Delta\mu_X = y$ and $\Delta\mu_Y = -x$ are the corresponding solutions when the hardnesses are $\eta_X = b$ and $\eta_Y = a$. In the present context, this implies that:

$$\Delta\mu_{Y_{\sigma'}}^{\sigma\sigma'} = -\Delta\mu_{X_{\sigma'}}^{\sigma'\sigma}$$
$$\Delta\mu_{X_\sigma}^{\sigma\sigma'} = -\Delta\mu_{Y_\sigma}^{\sigma'\sigma} \tag{36}$$

Thus, taking $\Delta\mu_{A_h}^{hs} = x > 0$ and $\Delta\mu_{B_s}^{hs} = -y < 0$, the denominator of Eq. (30) reads:

$$q_{hs}q_{sh} = \left\{ \begin{array}{c} \left[1 + \exp\left(-\beta\frac{\eta_h}{2}\right)\left[\exp(\beta x) + \exp(-\beta x)\right]\right] \times \\ \left[1 + \exp\left(-\beta\frac{\eta_s}{2}\right)\left[\exp(\beta y) + \exp(-\beta y)\right]\right] \end{array} \right\}^2 \tag{37}$$

Then, $Q_2 > 1$ if:

$$\left[\frac{1 + \exp\left(-\beta\frac{\eta_h}{2}\right)\left[\exp(\beta r) + \exp(-\beta r)\right]}{1 + \exp\left(-\beta\frac{\eta_h}{2}\right)\left[\exp(\beta x) + \exp(-\beta x)\right]}\right]$$
$$\times \left[\frac{1 + \exp\left(-\beta\frac{\eta_s}{2}\right)\left[\exp(\beta r) + \exp(-\beta r)\right]}{1 + \exp\left(-\beta\frac{\eta_s}{2}\right)\left[\exp(\beta y) + \exp(-\beta y)\right]}\right] > 1 \tag{38}$$

Since $|m| > |n| \Rightarrow \exp(\beta m) + \exp(-\beta m) > \exp(\beta n) + \exp(-\beta n)$, this inequality will be immediately true if $r > x$ and $r > y$. However, since:

$$x + y = 2r \tag{39}$$

this will never be the case, and we need to go further with the proof.

Before continuing, and for more clarity, let us rewrite Eq. (28) with the present variables:

$$\exp\left(-\beta\frac{\eta_h}{2}\right)\left[\exp(\beta x) - \exp(-\beta x)\right]$$
$$+ \exp\left(-\beta\frac{\eta_s}{2}\right)\left[\exp(-\beta y) - \exp(\beta y)\right] + 2\exp\left[-\beta\left(\frac{\eta_h + \eta_s}{2}\right)\right]$$
$$\left\{\exp[\beta(x - y)] - \exp[-\beta(x - y)]\right\} = 0 \tag{40}$$

In this form, it is easy to see that $\eta_h > \eta_s \Rightarrow x > y$.

Expanding the numerator and denominator of Eq. (38), and subtracting the latter from the former, we obtain:

$$\sqrt{q_{hh}q_{ss}} - \sqrt{q_{hs}q_{sh}} = R_1 - R_2 \tag{41}$$

with:

$$R_1 = \exp\left[\beta\left(r - \frac{\eta_s}{2}\right)\right] + \exp\left[-\beta\left(\frac{\eta_s}{2} + r\right)\right] + \exp\left[\beta\left(r - \frac{\eta_h}{2}\right)\right]$$
$$+ 2\exp\left[-\beta\left(\frac{\eta_h + \eta_s}{2}\right)\right] + \exp\left[-\beta\left(r + \frac{\eta_h}{2}\right)\right] \tag{42}$$

$$R_2 = \exp\left[\beta\left(y - \frac{\eta_s}{2}\right)\right] + \exp\left[-\beta\left(\frac{\eta_s}{2} + y\right)\right]$$
$$+ \exp\left[\beta\left(x - \frac{\eta_h}{2}\right)\right] + \exp\left[\beta\left(x - y - \frac{\eta_h + \eta_s}{2}\right)\right]$$
$$+ \exp\left[-\beta\left(\frac{\eta_h}{2} + x\right)\right] + \exp\left[\beta\left(y - x - \frac{\eta_h + \eta_s}{2}\right)\right] \tag{43}$$

According to Eq. (40), we can rewrite R_2 as:

$$R_2 = 2\exp\left[\beta\left(y - \frac{\eta_s}{2}\right)\right] + \exp\left[-\beta\left(\frac{\eta_h}{2} + x\right)\right]$$
$$+ 3\exp\left[\beta\left(y - x - \frac{\eta_h + \eta_s}{2}\right)\right] - \exp\left[\beta\left(x - y - \frac{\eta_h + \eta_s}{2}\right)\right] \tag{44}$$

Up to this point, we have been working with an arbitrary temperature. However, the presence of the exponential functions in our working expressions implies that the vast majority of the processes in which we apply the HSAB rule can be considered to occur at very low temperatures. Then, we could formally take the limit $\beta \to \infty$ in Eqs. (42) and (44). We must take into account that, since r, x, y, η_h, and η_s are greater than 0, all the exponentials with a -1 common factor in their arguments will tend to 0 more rapidly than the others when β increases. Therefore, they can be eliminated in the 0 temperature limit version of the above equations. Since, as previously noted, $x > y$, this same argument can be applied to neglect the term $\exp\left[\beta\left(y - x - \frac{\eta_h + \eta_s}{2}\right)\right]$. After these simplifications, we obtain the following expression:

$$
\begin{aligned}
R_1 - R_2 = {} & \exp\left[\beta\left(r - \frac{\eta_s}{2}\right)\right] + \exp\left[\beta\left(r - \frac{\eta_h}{2}\right)\right] \\
& + \exp\left[\beta\left(x - y - \frac{\eta_h + \eta_s}{2}\right)\right] - 2\exp\left[\beta\left(y - \frac{\eta_s}{2}\right)\right]
\end{aligned}
\tag{45}
$$

Now, we just have to notice that:

$$
\begin{aligned}
\left(R_1 - R_2\right)\exp\left[-\beta\left(r - \frac{\eta_s}{2}\right)\right] > {} & 1 + \exp\left[\beta\left(\frac{\eta_s - \eta_h}{2}\right)\right] \\
& - 2\exp\left[\beta\left(\frac{y - x}{2}\right)\right]
\end{aligned}
\tag{46}
$$

Then, since in the $\beta \to \infty$ (or, equivalently, in the $T \to 0$) limit the final two terms tend to 0, we have:

$$
R_1 - R_2 > 0
\tag{47}
$$

Subsequently, substituting this in Eqs. (41) and (30) is enough to see that $Q_2 > 1$, which completes the proof of the HSAB rule. We remark that this result only holds for sufficiently "low" temperatures, but according to recent results, this means temperatures up to 10^4 K [49, 60].

3 Conclusions

The previous discussion shows how to derive the HSAB rule within the finite-temperature GC formalism. This approach bypasses the need to consider the quadratic model for the energy as a function of electron number, thereby providing a stronger support for the validity of this principle. This work is close in spirit to recent developments on the foundations of c-DFT, where it has been argued about the convenience of extending the traditional zero-temperature descriptors to finite temperatures in a way that preserves their physical meaning [55]. The key ingredient is the definition of these descriptors as derivatives of the Helmholtz free energy.

On the other hand, we showed that we need to be more careful about the underlying conditions for which the HSAB rule holds. For example, we noticed that for sufficiently high temperatures, this principle may not hold. This is in line with previous findings regarding the validity of the maximum hardness and minimum electrophilicity principles. As in these previous cases, we remark the convenience of defining the finite-temperature descriptors using the Helmholtz free energy instead of the (internal) energy, as this preserves the physical meaning of their zero-temperature counterparts.

References

1. Pearson RG (1963) Hard and soft acids and bases. J Am Chem Soc 85:3533–3539
2. Pearson RG (1966) Acids and bases. Science 151:172–177
3. Pearson RG (1967) Hard and soft acids and bases. ChemBr 3(3):103–107
4. Ayers PW (2005) An elementary derivation of the hard/soft-acid/base principle. J Chem Phys 122:141102
5. Ayers PW, Parr RG, Pearson RG (2006) Elucidating the hard/soft acid/base principle: a perspective based on half-reactions. J Chem Phys 124:194107
6. Cardenas C, Ayers PW (2013) How reliable is the hard-soft acid-base principle? An assessment from numerical simulations of electron transfer energies. PCCP 15(33):13959–13968. https://doi.org/10.1039/c3cp51134k
7. Ayers PW, Cardenas C (2013) Communication: a case where the hard/soft acid/base principle holds regardless of acid/base strength. J Chem Phys 138:181106
8. Ayers PW (2007) The physical basis of the hard/soft acid/base principle. Faraday Discuss 135:161–190
9. Chattaraj PK, Lee H, Parr RG (1991) HSAB principle. J Am Chem Soc 113:1855–1856
10. Gazquez JL, Mendez F (1994) The hard and soft acids and bases principle: an atoms in molecules viewpoint. J Phys Chem 98:4591–4593
11. Mendez F, Gazquez JL (1994) Chemical-reactivity of enolate ions: the local hard and soft acids and bases principle viewpoint. J Am Chem Soc 116:9298–9301
12. Parr RG, Yang W (1989) Density-functional theory of atoms and molecules. Oxford UP, New York
13. Chermette H (1999) Chemical reactivity indexes in density functional theory. J Comput Chem 20:129–154
14. Geerlings P, De Proft F, Langenaeker W (2003) Conceptual density functional theory. Chem Rev 103:1793–1873
15. Ayers PW, Parr RG (2000) Variational principles for describing chemical reactions: The Fukui function and chemical hardness revisited. J Am Chem Soc 122:2010–2018
16. Ayers PW, Parr RG (2001) Variational principles for describing chemical reactions. Reactivity indices based on the external potential. J Am Chem Soc 123:2007–2017
17. Ayers PW, Anderson JSM, Bartolotti LJ (2005) Perturbative perspectives on the chemical reaction prediction problem. Int J Quantum Chem 101:520–534

18. Johnson PA, Bartolotti LJ, Ayers PW, Fievez T, Geerlings P (2012) Charge density and chemical reactivity: *a* unified view from conceptual DFT". In: Gatti C, Macchi P (eds) Modern charge density analysis. Springer, New York, pp 715–764

19. Chattaraj PK (ed) (2009) Chemical reactivity theory: a density functional view. CRC Press, Boca Raton, Florida

20. Liu SB (2009) Conceptual density functional theory and some recent developments. Acta Phys Chim Sin 25:590–600

21. Gazquez JL (2008) Perspectives on the density functional theory of chemical reactivity. J Mex Chem Soc 52:3–10

22. Miranda-Quintana RA (2018) Density functional theory for chemical reactivity. In: Islam N, Kaya S (eds) Conceptual density functional theory and its applications in the chemical domain. Apple Academic Press, Hamilton

23. Fuentealba P, Cárdenas C (2015) Density functional theory of chemical reactivity. In: Springborg M (ed) Chemical modelling, vol 11. The Royal Society of Chemistry, London, pp 151–174

24. Chattaraj PK, Ayers PW (2005) The maximum hardness principle implies the hard/soft acid/base rule. J Chem Phys 123:086101

25. Chattaraj PK, Ayers PW, Melin J (2007) Further links between the maximum hardness principle and the hard/soft acid/base principle: insights from hard/soft exchange reactions. PCCP 9:3853–3856

26. Miranda-Quintana RA (2017) The minimum electrophilicity and the hard/soft acid/base principles. J Chem Phys 146:046101

27. Parr RG, Chattaraj PK (1991) Principle of maximum hardness. J Am Chem Soc 113:1854–1855

28. Parr RG, Donnelly RA, Levy M, Palke WE (1978) Electronegativity: the density functional viewpoint. J Chem Phys 68:3801–3807

29. Parr RG, Pearson RG (1983) Absolute hardness: companion parameter to absolute electronegativity. J Am Chem Soc 105:7512–7516

30. Cardenas C, Ayers PW, De Proft F, Tozer DJ, Geerlings P (2011) Should negative electron affinities be used for evaluating the chemical hardness? PCCP 13:2285–2293

31. Cardenas C, Heidar Zadeh F, Ayers PW (2016) Benchmark values of chemical potential and chemical hardness for atoms and atomic ions (including unstable anions) from the energies of isoelectronic series. PCCP 18:25721–25734

32. Heidar Zadeh F, Richer M, Fias S, Miranda-Quintana RA, Chan M, Franco-Pérez M, Gonzalez-Espinoza CE, Kim TD, Lanssens C, Patel AHG, Yang XD, Vohringer-Martinez E, Cardenas C, Verstraelen T, Ayers PW (2016) An explicit approach to conceptual density functional theory descriptors of arbitrary order. Chem Phys Lett 660:307–312

33. Ayers PW (2007) On the electronegativity nonlocality paradox. Theor Chem Acc 118:371–381

34. Fuentealba P, Cardenas C (2013) On the exponential model for energy with respect to number of electrons. J Mol Model 19:2849–2853

35. Parr RG, Bartolotti LJ (1982) On the geometric mean principle for electronegativity equalization. J Am Chem Soc 104:3801–3803

36. Fuentealba P, Parr RG (1991) Higher-order derivatives in density-functional theory, especially the hardness derivative. J Chem Phys 94:5559–5564

37. Miranda-Quintana RA, Ayers PW (2018) Grand-canonical interpolation models. In: Islam N, Kaya S (eds) Conceptual density functional theory and its applications in the chemical domain. Apple Academic Press, Hamilton

38. Miranda-Quintana RA, Ayers PW (2016) Interpolation of property-values between electron numbers is inconsistent with ensemble averaging. J Chem Phys 144:244112

39. Heidar Zadeh F, Miranda-Quintana RA, Verstraelen T, Bultinck P, Ayers PW (2016) When is the Fukui function not normalized? The danger of inconsistent energy interpolation models in density functional theory. J Chem Theory Comp 12:5777–5787

40. Perdew JP, Parr RG, Levy M, Balduz JL Jr. (1982) Density-functional theory for fractional particle number: derivative discontinuities of the energy. Phys Rev Lett 49:1691–1694

41. Yang WT, Zhang YK, Ayers PW (2000) Degenerate ground states and fractional number of electrons in density and reduced density matrix functional theory. Phys Rev Lett 84:5172–5175

42. Ayers PW (2008) The continuity of the energy and other molecular properties with respect to the number of electrons. J Math Chem 43:285–303

43. Bochicchio RC, Rial D (2012) Note: energy convexity and density matrices in molecular systems. J Chem Phys 137:226101

44. Bochicchio RC, Miranda-Quintana RA, Rial D (2013) Communication: Reduced density matrices in molecular systems: grand-canonical electron states. J Chem Phys 139(19):191101. https://doi.org/10.1063/1.4832495

45. Miranda-Quintana RA, Bochicchio RC (2014) Energy dependence with the number of particles: density and reduced density matrices functionals. Chem Phys Lett 593:35–39. https://doi.org/10.1016/j.cplett.2013.12.071

46. Mermin ND (1965) Thermal properties of the inhomogeneous electron gas. PhysRev 137:A1441–A1443

47. Franco-Pérez M, Ayers P, Gazquez JL, Vela A (2015) Local and linear chemical reactivity responsefunctions at finite temperature in density functional theory. J Chem Phys 143:244117

48. Franco-Pérez M, Gazquez JL, Ayers P, Vela A (2015) Revisiting the definition of electronic chemical potential, chemical hardness, and softness at finite temperatures. J Chem Phys 143:154103

49. Franco-Pérez M, Heidar-Zadeh F, Ayers PW, Gazquez JL, Vela A (2017) Going beyond the three-states ensemble model: the electronic chemical potential and Fukui function for the general case. PCCP 19:11588–11602

50. Franco-Pérez M, Ayers PW, Gazquez JL, Vela A (2017) Local chemical potential, local hardness, and dual descriptors in temperature dependent chemical reactivity theory. PCCP 19:13687–13695

51. Polanco-Ramírez CA, Franco-Pérez M, Carmona-Espíndola J, Gazquez JL, Ayers PW (2017) Revisiting the definition of local hardness and hardness kernel. PCCP 19:12355–12364

52. Miranda-Quintana RA, Ayers PW (2016) Fractional electron number, temperature, and perturbations in chemical reactions. PCCP 18:15070–15080

53. Miranda-Quintana RA, Ayers PW (2016) Charge transfer and chemical potential in 1,3-dipolar cycloadditions. Theor Chem Acc 135:172

54. Miranda-Quintana RA, González MM, Ayers PW (2016) Electronegativity and redox reactions. PCCP 18:22235–22243

55. Miranda-Quintana RA (2017) Thermodynamic electrophilicity. J Chem Phys 146:214113

56. Miranda-Quintana RA, Chattaraj PK, Ayers PW (2017) Finite temperature grand canonical ensemble study of the minimum electrophilicity principle. J Chem Phys 147:124103

57. Malek A, Balawender R (2015) Revisiting the chemical reactivity indices as the state function derivatives. The role of classical chemical hardness. J Chem Phys 142:054104. https://doi.org/10.1063/1.4906555

58. Franco-Pérez M, Gazquez JL, Ayers PW, Vela A (2017) Thermodynamic hardness and the maximum hardness principle. J Chem Phys 147:074113

59. Chattaraj PK, Liu GH, Parr RG (1995) The maximum hardness principle in the Gyftopoulos-Hatsopoulos three-level model for an atomic or molecular species and its positive and negative ions. Chem Phys Lett 237:171–176

60. Chattaraj PK, Cedillo A, Parr RG (1996) Chemical softness in model electronic systems: dependence on temperature and chemical potential. ChemPhys 204:429–437