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THE INSTANTANEOUS IMAGE EFFECT: A NOVEL CONTRIBUTION TO THE MECHANISM OF HETEROGENEOUS CATALYSIS *

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A novel contribution to the mechanism of heterogeneous catalysis is discussed for a model H_2-on-nickel (100) system. The effect, which corresponds in a first approximation to the dispersion energy between adsorbate molecule and metal, is calculated through (1) admixture of an ionic component in the wave function of the adsorbate; (2) interaction between this ionic component and the image dipole which it creates in the polarizable metal. A single VB model, using an Anderson-type evaluation of the delocalization energy between adsorbate and metal, shows the image contribution to be 10 to 15% of the total adsorbate ↔ metal interaction energy.

Keywords: Hydrogen chemisorption theory on nickel, mechanism of heterogeneous catalysis, ionic component role of adsorbate, wave-function in surface bonding, image dipole interaction with ionic, component of adsorbate wave function

1. Introduction

The mechanism of heterogeneous catalysis has long been a stimulating puzzle for physicists and chemists alike [1]. Almost all approaches have used mono-electronic schemes (for an exception see [2]). Yet, since the electrons in metals are highly mobile, it is interesting to seek whether *electron correlation* effects between adsorbate and metal could play a significant role.

For example "instantaneous" or "dynamical" excitation in dihydrogen H_2 leads from

$H—H$ to $H^+—H^-$

and one may ask the legitimate question whether such an instantaneous dipole, in the excited "ionic" state of the adsorbate, can drive the electrons of the metal to arrange themselves in a manner which stabilizes the overall system. The answer is

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yes: the ionic state will polarize the metal and create an *image dipole*. It suffices that the metal electrons be able to follow the fluctuating dipole of the adsorbate. We shall show that the corresponding energy represents 13.5% of the overall stabilization energy at a point near the transition state for adsorbate dissociation.

2. Model

We use a valence-bond model. We first consider the isolated H_2 molecule. We build a ground singlet state and an excited singlet state by diagonalizing a 2-by-2 matrix for interaction between the purely covalent component and the purely ionic components:

$$\begin{array}{c|cc|} & \textit{covalent} & \textit{ionic} \\ \textit{covalent} & \text{diag.energy} - E & \text{mixing} \\ \textit{ionic} & \text{mixing} & \text{diag. energy} - E \end{array} = 0. \qquad (1)$$

The solutions of (1) are the extremely well-known energies of ground and first-excited singlet states of H_2. We therefore extract from these solutions the numerical values of the mixing energies.

In a second step we return to the same determinant which we "dress" by including, in the diagonal terms:

(a) the overlap-dependent effects, namely repulsion and delocalization effects, which are treated in an Anderson-type approach, using the best known "metal ↔ H atom" potential curves;

(b) the heretofore neglected but large polarization of the metal by the dipole in the ionic component of H_2.

The dressed 2-by-2 matrix looks as follows

$$\begin{array}{c|ll|} & \qquad\textit{covalent} & \qquad\textit{ionic} \\ \textit{covalent} & \begin{array}{l}\text{diag. energy (isolated } H_2\text{)} \\ +\text{overlap stabilization} \\ \text{due to metal} - E\end{array} & \text{mixing} \\ \textit{ionic} & \text{mixing} & \begin{array}{l}\text{diag. energy (isolated } H_2\text{)} \\ +\text{overlap stabilization} \\ \text{due to metal} + \textit{image energy} - E\end{array} \end{array} = 0 \qquad (2)$$

where the mixing terms have been calculated above.

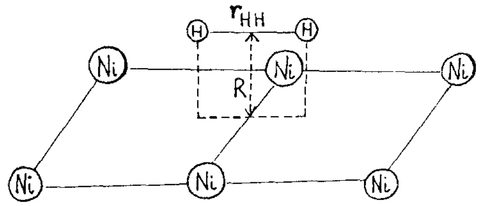

Fig. 1. Geometry of approach of adsorbed H_2 molecule or Ni (100) face.

The procedure is applied to a succession of geometries, with H_2 parallel to the surfaces and bridging the hollow nickel sites (see fig. 1) in which the HH distance r_{HH} is stretched from 1.4 a.u. (0.74 Å) to 3.4 a.u. by 0.5 a.u. intervals, while the distance $R_{H_2 \leftrightarrow \text{surface}}$ from the molecule to the plane takes the values 1.5, 1.25 or 1.00 Å, i.e. 2.835, 2.362 or 1.89 a.u. The results are plotted as 2-dimensional diagrams in fig. 2.

3. Details of the calculation

Let *a* and *b* be the best localized hydrogen 1s-type *orthogonal* atomic orbitals [3]. We have

$$\text{purely covalent component} = \frac{1}{\sqrt{2}}\left(a\bar{b} + b\bar{a}\right) \tag{3}$$

$$\text{purely ionic component} = \frac{1}{\sqrt{2}}\left(a\bar{a} + b\bar{b}\right). \tag{4}$$

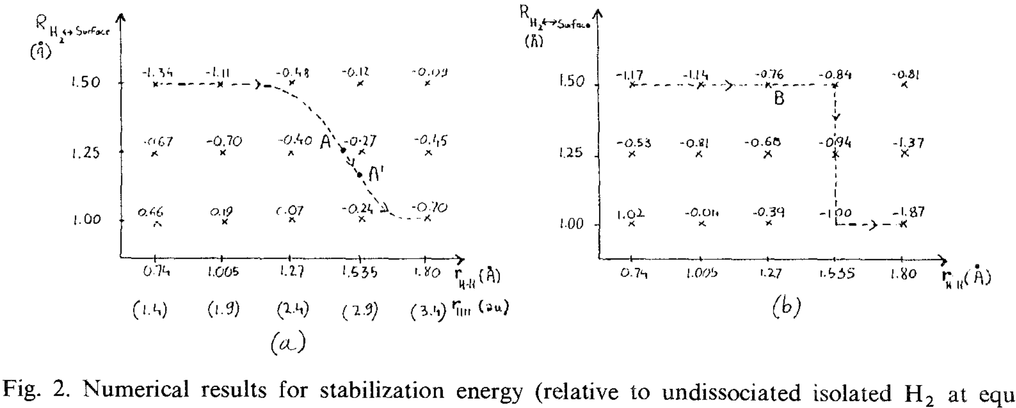

Fig. 2. Numerical results for stabilization energy (relative to undissociated isolated H_2 at equilibrium) of H_2 on Ni (100) face. (a) Parameter n evoluated from theoretical model [8], (b) Parameter n varied linearly from 1 ($r_{HH} = 1.40$ a.u.) to 2 (r_{HH}) = 3.40 a.u.). The regions of the transition state for heterogeneous dissociation are points A or A′ (case (a)) and B (case (b)).

Table 1
Mixing energies (eq. (1)) between purely covalent and purely ionic components of isolated H_2

r_{HH} (a.u.)	Mixing energy (a.u.)
1.40	0.4281
1.90	0.3241
2.40	0.2385
2.90	0.1724
3.40	0.1230

Throughout the calculation we neglect the exchange integral K_{ab} between a and b. In H_2, at the equilibrium internuclear distance $r_e = 1.4$ a.u., K_{ab} is 0.0117 a.u.; at $r_{HH} = 2.40$ a.u., it has already fallen to 0.0039 a.u. [3].

Thus we can equate the energy of $(a\bar{b} + b\bar{a})$ to that of $(a\bar{b} - b\bar{a})$ and the energy of $(a\bar{a} + b\bar{b})$ to that of $(a\bar{a} - b\bar{b})$. Then the energy of (3) is given by the well-known energy of the lowest ${}^3\Sigma_u^+$ curve of H_2 [4]; similarly the energy of (4) is given by the energy of the lowest excited ${}^1\Sigma_u^+$ curve of H_2 [5]:

$$E_{(\text{cov})} \approx E({}^3\Sigma_u^+) \tag{5}$$

$$E_{(\text{ionic})} \approx E({}^1\Sigma_u^+). \tag{6}$$

We can than construct the 2-by-2 determinant (1) for isolated H_2 by using (5) and (6) as diagonal terms. Now the lower root of the determinant must be the energy $E({}^1\Sigma_g^+)$ of ground state H_2 [4]. Working backward from the "experimental" energies of the ${}^1\Sigma_g^+$, ${}^1\Sigma_u^+$ and ${}^3\Sigma_u^+$ states we get the *mixing energies* of table 1.

We will use these same matrix elements in the second part of the calculation; only the *diagonal energies* will change. In other words we "dress" the VB matrix of H_2 by the effect of the metal.

We now repeat the calculation for a H_2 molecule adsorbed on a metal. The effects of the metal-hydrogen overlap–which is much smaller than the H-H

Table 2
Energies (cm^{-1}) of the Cu ↔ H diabatic triplet ${}^3\Sigma$ curve and adiabatic singlet ${}^1\Sigma$ curves (from ref. [7]).

$R_{Cu \leftrightarrow H}$ (a.u.)	${}^3\Sigma^+$	${}^1\Sigma^+$
3	10500	−19700
3.5	4000	−17200
4	1000	−13100
4.5	400	9600
5	~100	−6700
6	0	−3000

overlap at the distances under consideration–is treated according to the theory of magnetic Hamiltonians [6] which does not require an explicit orthogonalization. For that, we need numerical curves for the exclusion repulsion between hydrogen atoms and metal M atoms, and for the stabilization through hydrogen ↔ metal delocalization. We extract these from the potential curves for the MH diatomic molecule. Unfortunately, no such curves have been published for NiH, but they do exist for CuH [7].

The repulsion $W_{\mathrm{rep}}(r)$ is given directly by the *diabatic* triplet energy curve of fig. 3 of ref. [7] (see our table 2) which excludes any mixing with the d^9s^2 configuration:

$$W_{\mathrm{rep}}(r) = E(^3\Sigma^+). \tag{7}$$

The delocalization, which in a VB model corresponds to electron jumps from metal to hydrogen and vice versa, is given by the familiar Anderson model [6] for magnetic problems:

$$-\frac{1}{2}\frac{\langle \mathrm{Cu}\,\bar{h} + h\,\overline{\mathrm{Cu}}\,|\mathrm{H}|\,\mathrm{Cu}\overline{\mathrm{Cu}}\rangle^2}{\Delta E_1} - \frac{1}{2}\frac{\langle \mathrm{Cu}\,\bar{h} + h\,\overline{\mathrm{Cu}}\,|\mathrm{H}|\,h\bar{h}\rangle^2}{\Delta E_2} = -\frac{4t^2}{U}, \tag{8}$$

where U is some average excitation energy and t is the matrix element $\langle h\,|\mathrm{H}|\,\mathrm{Cu}\rangle$ (the β of the chemists). The ground-state *adiabatic* singlet energy (fig. 1 of ref. [7]; see table 2) is then given by

$$W_{\mathrm{rep}} - \frac{4t^2}{U} = E(^1\Sigma^+). \tag{9}$$

It is relatively easy to transfer these results to the interaction between a copper atom and a hydrogen atom-in-the *molecule* H_2. First of all, relative to eq. (9), the factor 4 is reduced to a factor 2 because of the random distribution of spins on the metallic surface (so that we must exclude the cases where the spin on the Cu atom and on its neighboring H atom are parallel). Second, whereas for an *isolated* H atom we have electron jumps which couple electronic states such as:

$$\begin{array}{ccccccccccc} \uparrow & & \downarrow & & \oplus & & \overset{\ominus}{\uparrow\downarrow} & & \downarrow & & \uparrow \\ \mathrm{Cu} & \ldots & \mathrm{H} & \leftrightsquigarrow & \mathrm{Cu} & \ldots & \mathrm{H} & \leftrightsquigarrow & \mathrm{Cu} & \ldots & \mathrm{H} \end{array}$$

for H-in-H_2 the factor 2 is reduced to 1 because the r.h. arrow is forbidden as it would change the overall spin of H_2:

$$\begin{array}{ccccccccccccccccc} \uparrow & & \downarrow & & \uparrow & & \oplus & & \overset{\ominus}{\uparrow\downarrow} & & \uparrow & & \downarrow & & \uparrow & & \uparrow \\ \mathrm{Cu} & \ldots & \mathrm{H} & - & \mathrm{H} & \leftrightsquigarrow & \mathrm{Cu} & \ldots & \mathrm{H} & - & \mathrm{H} & \not\leftrightsquigarrow & \mathrm{Cu} & \ldots & \mathrm{H} & - & \mathrm{H} \end{array}$$

Thus, making the further assumption that the curves for CuH are a good approximation to those for NiH, and using (7) and (9), we can write

$$\mathrm{Ni} \longleftrightarrow \mathrm{H}\ (\text{in purely covalent } H_2) = W_{\mathrm{rep}} - \frac{nt^2}{U} = \left(1 - \frac{n}{4}\right)E(^3\Sigma) + \frac{n}{4}E(^1\Sigma), \tag{10}$$

where n is an empirical parameter which must be 1 for short H–H distances and 2 for totally dissociated H_2. We have estimated the variation of n in two manners: (a) by extending our theoretical model [8]. This gives $n = 1.088$, 1.205, 1.355, 1.528 and 1.696 respectively for $r_{HH} = 1.4$, 1.9, 2.4, 2.9 and 3.4 a.u.; (b) by simple linear interpolation from $n = 1$ ($r = 1.4$ a.u.) to $n = 2$ ($r = 3.4$ a.u.).

For ionic H_2 both factors 1/2 apply and there is a further reduction to $t^2/(2U)$:

$$\mathrm{Ni} \longleftrightarrow \mathrm{H}\ (\text{in purely ionic } \mathrm{H}_2) = W - \frac{t^2}{2U} = \tfrac{7}{8}E(^3\Sigma^+) + \tfrac{1}{8}E(^1\Sigma^+). \qquad (11)$$

Indeed, the positively charged hydrogen atom has "zero"repulsion with the metal, while the negatively charged atom has "twice" as much repulsion as a neutral atom. Also the average excitation energy from $\mathrm{Cu}\ldots\overset{\oplus}{\mathrm{H}}\text{–}\overset{\ominus}{\mathrm{H}}$ to $\overset{\oplus}{\mathrm{Cu}}\ldots\mathrm{H}\text{–}\overset{\ominus}{\mathrm{H}}$ (or from $\mathrm{Cu}\ldots\overset{\ominus}{\mathrm{H}}\text{–}\overset{\oplus}{\mathrm{H}}$ to $\overset{\ominus}{\mathrm{Cu}}\ldots\mathrm{H}\text{–}\overset{\oplus}{\mathrm{H}}$) should be substantially larger than U (for $\mathrm{Cu}\ldots\mathrm{H}\overset{\uparrow}{\mathrm{H}}\text{–}\mathrm{H}\overset{\downarrow}{\mathrm{H}}$ to $\overset{\oplus}{\mathrm{Cu}}\ldots\overset{\ominus}{\mathrm{H}}\text{–}\overset{\downarrow}{\mathrm{H}}$ or to $\overset{\ominus}{\mathrm{Cu}}\ldots\overset{\oplus}{\mathrm{H}}\text{–}\overset{\downarrow}{\mathrm{H}}$) for covalent H_2. The factor 2 in the denominator of $t^2/(2U)$ accounts for this, and is also in agreement with the well-known MO feature that 1 or 3 electrons give half of the delocalization stabilization of 2 electrons.

4. Results

Fig. 2 shows the overall results for the 2 different variations of the parameter n. In both cases a path for dissociation exists (from adsorbed undissociated H_2 to dissociated H_2 bonded to metal) with *negative activation energy* relative to undissociated H_2 (for infinitely separated atoms the calculated energy is −1.91 eV). Experimentally the only known observable is the heat of chemisorption of two H atoms obtained by spontaneous dissociation of H_2 on a Ni(100) face: −0.98 eV [9]; the adsorption of *molecular* H_2 is not observed on nickel since the molecule dissociates. The final point of diagram (a), −0.70 eV, agrees quite well with this figure but the reaction path is uphill. The final point of diagram (b), −1.87 eV, is too low, but the calculated path is thermodynamically downhill, with an energy stabilization ($-1.87 + 1.17 = -0.70$ eV) close to the observed heat of chemisorption.

Let us consider a typical calculation for $r_{HH} = 2.4$ a.u., $R_{H_2 \leftrightarrow \text{surface}} = 1.25$ Å and n = theoretical estimate of 1.355. The purely covalent diagonal energy (−0.9379 a.u.) is stabilized by −0.1048 a.u. by overlap effects while the purely ionic diagonal energy (−0.7566 a.u.) has practically zero (+0.0019 a.u.) overlap stabilization energy but a significant −0.0459 a.u. image energy of interaction with the metal. The mixing element is 0.2385 a.u. (table 1). The final energy is −1.189 a.u., i.e. −0.40 eV below the undissociated isolated H_2 molecule (fig. 2) and *2.36 eV below isolated H_2 also stretched to 2.4 a.u.*. Of these 2.36 eV, the overlap contribution and image contributions are respectively 2.04 eV and 0.32

Table 3
Image effect stabilization (in eV) and (in parentheses) complete stabilization energy (with respect to H_2 at the same H–H distance). a) and b) refer to the two choices of n in eq. (10).

		r_{HH}				
$R_{H_2 \leftrightarrow \text{surf.}}$		a.u. 1.4	1.9	2.4	2.9	3.4
(Å)		Å 0.74	1.005	1.27	1.535	1.80
	1.5	−0.11 (−1.34)	−0.18 (−1.86)	−0.20 (−2.44)	−0.18 (−3.13)	−0.15 (−3.86)
a)	1.25	−0.20 (−0.67)	−0.28 (−1.45)	−0.32 (−2.36)	−0.27 (−3.28)	−0.20 (−4.22)
	1.0	−0.38 (+0.66)	−0.53 (−0.56)	−0.57 (−1.89)	−0.47 (−3.25)	−0.33 (−4.47)
	1.5	−0.12 (−1.17)	−0.18 (−1.85)	−0.19 (−2.72)	−0.16 (−3.85)	−0.11 (−4.58)
b)	1.25	−0.20 (−0.53)	−0.29 (−1.56)	−0.31 (−2.64)	−0.25 (−3.95)	−0.17 (−5.14)
	1.0	−0.35 (+1.02)	−0.51 (−0.79)	−0.53 (−2.35)	−0.42 (−4.01)	−0.28 (−5.64)

eV (13.5%) if they are included in that order (the image contribution is larger percentagewise if it is calculated first, whithout any overlap contribution).

Table 3 shows the image contribution (calculated after the delocalization contribution) for the whole set of geometries, together with the total stabilization energy. It is clear that the "instantaneous" or "dynamical" image effect always plays an important role.

5. Discussion

We have shown that the dynamical image effect, due to the instantaneous dipole ↔ image dipole interaction between adsorbate and metal, leads to a significant stabilization energy of the order of 0.3 eV to 0.5 eV. The image interaction increases roughly as the square of the length of the dissociating molecule and as the inverse cube distance to the metal surface. A few points still require discussion:

(1) The preceding formulation assumes an immediate response of the metal to the fluctuating dipole created by the movement of the electrons on the hydrogen molecules. This requires further detailed investigation, but we can already notice that

(a) There are 2 processes for fluctuation in H_2: a *slow* process in which $\underline{+\;-} \rightarrow \underline{-\;+}$ via coupling of the two ionic components through their exchange integral (0.0039 a.u. = 0.10 eV at $r_{HH} = 2.40$ a.u.), and a *fast* dominant process in which $a\bar{a}$ couples with $b\bar{b}$ *via* the covalent component. For this mechanism the coupling energy at $r_{HH} = 2.40$ a.u. is

$$\frac{\langle a\bar{a} | \mathrm{H} | a\bar{b} \rangle \langle a\bar{b} | \mathrm{H} | b\bar{b} \rangle}{0.9379 - 0.7566} \tag{13}$$

which is equal to $(0.1192)^2/0.1813 = 0.0784$ a.u. = 2.13 eV. This is smaller than the width of either d or s band; whence the possibility of resonance with metal plasmons of the same frequency.

(b) Moreover, we can estimate how well the electrons or holes near the Fermi surface follow the molecular electron-pair fluctuation, by comparing Fermi velocities (1.98×10^8 cm. s^{-1} in Fe; 1.57×10^8 cm. s^{-1} in Cu) [10] with the speed of the oscillating H_2 electrons. The transfer time from covalent to ionic component (2.13 eV coupling) is 0.31×10^{-15} s. Remembering that the electron covers a 1.27 Å distance, the speed of the electron is 0.41×10^8 cm.s^{-1}. This is of the same order of magnitude as, but somewhat smaller than, the speed of the Fermi electrons, which should therefore easily follow the fluctuations in the molecule. (A similar formulation, in time-independent language, could have been given in terms of wave lengths.)

(2) One may also question the validity of the use of the image charge at close distances because of the spill-over of metal electrons (which tends to move the mirror plane out of the surface) and of a certain saturation of opposite direction (which decreases the effective Coulomb potential due to the entrance of an isolated external electron into the Fermi sea) [11]. However, the spill-over effect tends to increase the image interaction while the overlap-dependent effects are included in our model.

(3) Other geometrical approaches–for instance H_2 *perpendicular* to the surface–yield much larger image energies [12]. However trial pathways of dissociation for such an approach do not yield reasonable potential curves with a transition state.

(4) The relative energies of different approaches might change if we could use Ni–H potentials, which should be softer than the Cu–H potentials.

(5) If our estimate of the image effect is correct, it implies that *ab initio* calculation of dissociative adsorption on clusters would improve by including both a sufficient number of atoms to reproduce the polarizability of the metal, and extensive configuration interaction to account correctly for the instantaneous polarization of the metal.

(6) The calculated stabilization of the ionic subcomponents by their interaction with their mirror images essentially corresponds to the dispersion energy between H_2 and the metal [13]. However, by comparison with the classical treatment of the dispersion energy (coupled single-excitations on H_2 and on the metal) we go one step further since we evaluate the *perturbed* ground-state wave function of H_2 and its new energy which includes higher-order terms.

(7) Our results bear some analogy to recent models [14] for polarizable molecules in polar solvents, in which the ionic component of the molecular wave functions are preferentially stabilized by the polarity (but not the polarizability) of the solvent. They are also analogous to Warshel's calculated stabilization [15] of ionic resonance forms at the active site in enzymatic reactions.

(8) Our calculations imply that the best routes for catalytic dissociation may be those which will stabilize, as much as possible, the lower excited ionic state(s) of reactant(s).

(9) One should not dismiss the possible generality of our mechanism. At a first glance, for instance, zeolites cannot create an image dipole. Yet in model calculations, Van Santen et al. have shown [16] that the O–H bonds in zeolites are highly polarizable, as indicated by the ease of proton transfer. These bonds may serve as a polarizable "pseudo-metallic" medium.

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[8] A complete treatment would include the indirect coupling of the neutral singlet component $(a\bar{b} + b\bar{a})\sqrt{2}$ with a symmetrical combination $(ab + \overline{ab})/\sqrt{2}$ of triplet states through the hydrogen molecule-metal charge transfer processes.

$$\mathrm{Me}\downarrow \ldots \mathrm{H}\uparrow - \mathrm{H}\downarrow \leftrightsquigarrow \overset{\ominus}{\mathrm{Me}\uparrow}\downarrow \ldots \overset{\oplus}{\mathrm{H}} - \mathrm{H}\downarrow \leftrightsquigarrow \mathrm{Me}\uparrow \ldots \mathrm{H}\uparrow - \mathrm{H}\uparrow .$$

One might treat the problem as a three-state problem, with a $2t^2/U$ coupling) for each metal atom) between the singlet neutral state and the triplet combination. Noticing however that this coupling results in a stabilization which is proportional to the weight λ^2 of the neutral singlet component in H_2 one may approximate this effect by considering a $(2\lambda^2)\times(-t^2/U)$ stabilization of the neutral singlet, where λ^2 is calculated before dressing and varies from $\frac{1}{2}(1+\epsilon)$ for short H–H distances to 1 for large interatomic distances. The non-linear variation of n in expression (10) reported in the text has been derived along this scheme.

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[12] For instance, for H_2 standing vertically above the hollow center of a Ni(100) face, with the closest H atom at 0.8 Å from the face and the molecule stretched to 2.4 a.u., the image energy is −0.0900 a.u. and contributes some 23% (0.67 eV) of the total stabilization energy (2.91 eV).

[13] Note that we further combine the separately stabilized subcomponents into the symmetric $(a\bar{a}+b\bar{b})$ component before diagonalization. We could have equally well accounted for the metal polarization by interacting $[(a\bar{a}+b\bar{b})\times$(ground-state function of the metal)] with doubly-excited configurations of the type $[(a\bar{a}-b\bar{b})\times$(single excitations on the metal)], and then performing the same 2-by-2 diagonalization.

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