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Inclusion of dynamic σ-π polarization in π-electron *ab initio* calculations

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Summary. A method is presented, whereby dynamic σ-π polarization, i.e. the correlation effect expressed by simultaneous (σ-σ^*, π-π^*) excitations, can be approximately included in a multi-reference configuration interaction (MRCI) or multi-configurational self-consistent field (MC-SCF) calculation, without need to explicitly correlate the sigma orbitals. The method, which we call the capacitance matrix method, is based on the use of conventional one-electron integrals, from which a σ polarization potential (SPP) contribution is computed and added to the one- and two-electron Hamiltonian. In the present form, the method requires one parameter for each type of atom, and one for each type of bond. These parameters were adjusted to reproduce the dynamic σ-π polarization energy, computed by restricted multi-reference CI calculations, of a number of states of different hydrocarbons, and the agreement was within a few percent. Using the same parameters in CAS (Complete Active Space) SCF calculations of various states of benzene gives excitation energies, when SPP is included, which is comparable to those obtained by much more elaborate MRCI calculations.

Key words: Dynamic σ-π polarization – MRCI – MC-SCF

1. Introduction

This paper presents an efficient way to improve *ab initio* calculations of certain molecules, by the approximate inclusion of some correlation effects, i.e., dynamic polarization, which involves orbitals that are not explicitly correlated. This method is primarily intended for π-bonded systems, but may be useful for other systems as well.

The long-standing interest in π-bonded systems has practical as well as theoretical reasons. Near-degeneracy of $\pi\pi^*$ states, together with many transitions with large transition moments, makes the photochemical and spectroscopic properties interesting. Thus, the present work was prompted by a study of excitation energies and transition moments in the nucleic acid base monomers [1]. Systems of this size, while very small from a biochemist's point of view, are at the upper limit of feasibility for a serious correlated treatment, and one is forced to make severe compromises if even larger systems are to be studied.

Since the qualitative aspects of the ground and $\pi\pi^*$ excited states are well described by correlation of the valence π electrons only, one is naturally tempted to take this as a starting point. Early π-electron theories assumed a separability of the σ and π subsystems, and treated explicitly only the latter in a minimal basis. Even such crude models were very successful in the qualitative prediction of the electronic structure of ground as well as $\pi\pi^*$ excited states, but quantitative predictions were of poor quality. The apparent success of Goeppert-Mayer and Sklar in reproducing the benzene excitation energies [2] was fortuitous, due to the neglect of a large number of electrostatic repulsion integrals. It was found by Pariser, in collaboration with Parr, that within what was later called the Zero Differential Overlap approximation, good quantitative agreement with experiment could be obtained, provided that electron repulsion integrals were treated as adjustable parameters. In particular, for carbon it was necessary to adopt a value of the $(2p_z 2p_z, 2p_z 2p_z)$ integral of ≈ 11 eV, in contrast to the value ≈ 17 eV obtained by actually computing this integral with a reasonable $2p$ orbital [3].

If one wants to retain the *ab initio* level, and still take advantage of the inert nature of the σ skeleton, it is natural to attempt to include more dynamic correlation in the π system, while merely optimizing the occupied σ orbitals without correlating them. This is conveniently done by a Complete Active Space (CAS) SCF calculation [4] with all valence π active, and using the resulting orbitals in a subsequent Multi-reference CI (MRCI) correlating all the π electrons. Unfortunately, this turns out to be insufficient.

Of course, the next natural thing is to include single and double excitations from the σ orbitals. This requires an MRCI calculation with a carefully selected reference space, and the resulting number of configurations is usually too large to allow this. Moreover, when ionic states are involved, it may be difficult to provide suitable orbitals to the MRCI: The inadequate treatment of dynamic correlation in the orbital optimization step results in use of inappropriate orbitals in the subsequent MRCI.

This is neatly exemplified by studies of ethene [5–7], which is small enough to allow extensive MRCI calculations. Here, the lowest singlet $\pi\pi^*$ state, the so-called V state (Herzberg), is strongly ionic and can be described as a "resonance" structure, $C^+C^- \leftrightarrow C^-C^+$. If orbitals are optimized without allowing enough dynamic correlation, the π^* orbital expands considerably. Extensive MRCI calculations suggest an optimal π^* orbital to have the spatial extent $\langle z^2 \rangle \approx 7.8$ a.u. [7], where z is the distance from the molecular plane. While this is large as compared to an ordinary π orbital, it is much smaller than the value obtained for the RHF π^* orbital (≈ 20 a.u.).

A more demanding example is benzene, where only rather limited CI expansions can be afforded [8]. A valence π CASSCF gives excitation energies in reasonable agreement with experiment for the $^1B_{2u}$ and $^1E_{2g}$ states, but more than 1 eV too high for the $^1B_{1u}$ and $^1E_{1u}$ states. The first two are ordinary covalent states, while the other two are ionic. State-specific orbitals, taken from the CASSCF calculations, were used in subsequent internally contracted CI (CCI) calculations, correlating σ as well as π orbitals. (The CCI is an MRCI method, where the full set of independent configuration functions have been replaced with a much smaller set of linear combinations [9].) The z^2 expectation value of the e_{2u} CCI natural orbital, which is around 2 for the first two states, climbs to 6 for the $^1B_{1u}$ state and no less than 16 for the $^1E_{1u}$ state – halfway to the 32 a.u. typical of a Rydberg orbital. The energy errors are reduced, but by no means removed, by the CCI calculation.

Table 1. Important configurations and their coefficients in an MR-SDCI wave function for the V state of ethene, using natural orbitals[a]

Configuration	Coefficient
$\ldots(1\pi)^1(1\pi^*)^1$	0.9336
$1\pi^*, 3a_g \rightarrow 1\pi, 3b_{1u}$	−0.1007
$1\pi, 3a_g \rightarrow 1\pi^*, 3b_{1u}$	0.0713
$1\pi^*, 1b_{3g} \rightarrow 1\pi, 2b_{3u}$	−0.0644
$1\pi, 1\pi^* \rightarrow 2\pi, 2\pi^*$	0.0643
$1\pi^*, 1b_{3g} \rightarrow 1\pi, 3b_{3u}$	−0.0625
$1\pi^*, 2b_{1u} \rightarrow 1\pi, 4a_g$	−0.0523
$1\pi, 3a_g \rightarrow 2\pi^*, 3b_{1u}$	−0.0433

[a] R. Lindh and B. O. Roos, Int. J. Quantum Chem. 35, 813 (1989)

Returning now to the ethene calculation, Table 1 contains a listing of the largest CI coefficients of the V state (using natural orbitals). The table shows that, next to the leading $\pi\pi^*$ configuration, the wave function is dominated by the $(\sigma\sigma^*, \pi\pi^*)$ and $(\sigma\sigma^*, \pi^*\pi)$ excitations. From many other cases, we know that such excitations are in fact typical of ionic states, and play a lesser rôle for purely covalent states. Therefore, we may assume that a major *differential* dynamic correlation effect stems from these excitations, which is readily understood in terms of the dynamic polarization of the σ skeleton, by the fluctuation potential from the π electrons. Such an effect can be mimicked in a π-electron calculation by adding a polarization potential contribution to the one- and two-electron interaction integrals. This "Sigma Polarization Potential" (SPP) contribution can in principle be determined in terms of an effective hamiltonian from a more elaborate MRCI, but such a procedure, unless approximated somehow, would negate the purpose of replacing the calculation by a cheaper π-electron treatment. We hope to demonstrate the possibility to express the SPP by conventional interaction integrals. The approximation investigated in this paper may be called, for reasons to appear, the Capacitance Matrix Model. This method requires determination of one parameter for each atom type, and one for each bond type. It is too early to enter into speculations on transferability, but in the cases where we can compare to more extensive MRCI calculations, the SPP effect is reproduced within a few percent. If this holds in general, there would not be much point in refining the model further, since then other, neglected effects would dominate the remaining error.

2. The capacitance matrix model

If the σ system is replaced by a polarizable medium, which responds instantaneously to an external perturbing electrostatic potential V, then to second order in energy:

$$E = E_0 + \int \varrho^\sigma(\mathbf{r}) V(\mathbf{r})\, dv - \tfrac{1}{2} \int\int \kappa^\sigma(\mathbf{r}_1, \mathbf{r}_2) V(\mathbf{r}_1) V(\mathbf{r}_2)\, dv_1 \qquad (1)$$

where ϱ^σ is the charge density of the σ electrons, and κ^σ is a static distributed susceptibility function.

The last term is the energy gained by polarization of the σ system. We define this as the SPP energy, and it can be approximated to any required accuracy by:

$$E_{\mathrm{SPP}} = -\tfrac{1}{2}\sum_{KL} X_{KL} V(\boldsymbol{R}_K) V(\boldsymbol{R}_L) \tag{2}$$

where X_{KL} is a symmetric matrix. A uniform shift of potential reference does not affect the system, so we must require:

$$\sum_K X_{KL} = \sum_L X_{KL} = 0 \tag{3}$$

Equation (2) can be made an exact relation, if the degrees of freedom of V is finite, by proper choice of X_{KL} and $\boldsymbol{R}_K$. A dimensional analysis shows that the elements X_{KL} are capacitances, and we call this the capacitance matrix method.

If the perturbing potential arises from a system of π electrons, it acts as an operator:

$$\hat{V}(\boldsymbol{R}) = \int \hat{\varphi}^\dagger(\boldsymbol{r}) \frac{1}{|\boldsymbol{R} - \boldsymbol{r}|} \hat{\varphi}(\boldsymbol{r})\, dv \tag{4}$$

if $\varphi(\boldsymbol{r})$ is the annihilator field operator of the π electrons. Insertion in Eq. (2) replaces the relaxation energy by the operator:

$$\begin{aligned}\hat{U}_{\mathrm{SPP}} &= -\tfrac{1}{2}\sum_{KL} X_{KL} \iint \hat{\varphi}^\dagger(\boldsymbol{r}_1) \frac{1}{|\boldsymbol{R}_K - \boldsymbol{r}_1|} \hat{\varphi}(\boldsymbol{r}_1) \hat{\varphi}^\dagger(\boldsymbol{r}_2) \frac{1}{|\boldsymbol{R}_L - \boldsymbol{r}_2|} \hat{\varphi}(\boldsymbol{r}_2)\, dv_1\, dv_2 \\ &= -\tfrac{1}{2}\sum_{KL} X_{KL} \iint \hat{\varphi}^\dagger(\boldsymbol{r}_1) \hat{\varphi}^\dagger(\boldsymbol{r}_2) \frac{1}{|\boldsymbol{R}_K - \boldsymbol{r}_1|} \frac{1}{|\boldsymbol{R}_L - \boldsymbol{r}_2|} \hat{\varphi}(\boldsymbol{r}_2) \hat{\varphi}(\boldsymbol{r}_1)\, dv_1\, dv_2 \\ &\quad -\tfrac{1}{2}\sum_{KL} X_{KL} \int \hat{\varphi}^\dagger(\boldsymbol{r}) \frac{1}{|\boldsymbol{R}_K - \boldsymbol{r}|} \frac{1}{|\boldsymbol{R}_L - \boldsymbol{r}|} \hat{\varphi}(\boldsymbol{r})\, dv\end{aligned} \tag{5}$$

acting on the π electron system.

In a given orbital basis $\{\varphi_t\}$, the two-electron matrix elements of $\hat{U}_{\mathrm{SPP}}$ are trivial:

$$(tu|vx)_{\mathrm{SPP}} = -\tfrac{1}{2}\sum_{KL} X_{KL} \langle \varphi_t | \frac{1}{|\boldsymbol{R}_K - \boldsymbol{r}|} | \varphi_u \rangle \langle \varphi_v | \frac{1}{|\boldsymbol{R}_L - \boldsymbol{r}|} | \varphi_x \rangle \tag{6}$$

The one-electron matrix elements are:

$$\langle t | \hat{U}^{(1)}_{\mathrm{SPP}} | u \rangle = -\tfrac{1}{2}\sum_{KL} X_{KL} \langle \varphi_t | \frac{1}{|\boldsymbol{R}_K - \boldsymbol{r}|} \frac{1}{|\boldsymbol{R}_L - \boldsymbol{r}|} | \varphi_u \rangle \tag{7}$$

which can be conveniently approximated as:

$$\langle t | \hat{U}^{(1)}_{\mathrm{SPP}} | u \rangle = -\tfrac{1}{2}\sum_{KL} X_{KL} \sum_x \langle \varphi_t | \frac{1}{|\boldsymbol{R}_K - \boldsymbol{r}|} | \varphi_x \rangle \langle \varphi_x | \frac{1}{|\boldsymbol{R}_L - \boldsymbol{r}|} | \varphi_u \rangle \tag{8}$$

The only integrals that appear are trivial one-electron integrals of the same type as the nuclear attraction. Equations (6) and (8) can give any required accuracy, provided suitable points $\boldsymbol{R}_K$ and integration weight X_{KL} are used, together with an adequate orbital basis, for any SPP correction of the instantaneous linear response type.

In order to have a simple model, we make the further approximation of placing the points at the atomic nuclei. If this is done, then Eq. (2) is fully equivalent to the electrostatic energy of a capacitor network, with one node for each atom, as follows: Let the additional charge at each node, due to the perturbing potential, be Q_K. Then the energy to be minimized is:

$$E = \tfrac{1}{2} \sum_{KL} \frac{Q_K Q_L}{C_{KL}} + \sum_K Q_K V_K \tag{9}$$

with the additional constraint that:

$$\sum_K Q_K = 0$$

Minimization gives precisely the energy in Eq. (2), provided that suitable coefficients are chosen, and assuming that the matrix X_{KL} fulfills Eq. (3). The coefficients have the physical dimensions of reciprocal capacitances, and they are related to the coefficients X_{KL} by:

$$\begin{aligned} X_{KL} &= \frac{g_K g_L}{2\alpha} - (A^{-1})_{KL} \\ A_{KL} &= \frac{1}{C_{KL}} \\ g_K &= \sum_L A_{KL} \\ \alpha &= \sum_K g_K \end{aligned} \tag{10}$$

Equation (2) and Eq. (9) are equivalent if Eqs. (10) hold, and the significance of Eq. (9) is that the quantities $1/C_{KL}$ have a simple physical interpretation. $1/C_{KK}$ expresses the energy expended to alter the σ charge of atom K from its optimal value, while $1/C_{KL}$ represents the interaction of σ charges on different atoms K and L. Thus, to a first approximation, we can simply assume $1/C_{KK}$ to be transferable atomic quantities, and use $1/C_{KL} \approx 1/R_{KL}$, the reciprocal interatomic distance.

We have tested this hypothesis in actual calculations, and found it to work fairly well. It is interesting to note that the $(\pi_u\pi_u, \pi_u\pi_u)$ and $(\pi_g\pi_g, \pi_g\pi_g)$ integrals are both reduced from 16.2 eV to 11.5 eV, similar to the reduction in carbon one-center integrals suggested by Pariser [3]. A similar reduction was also recently reported in a theoretical study, where an effective hamiltonian for the π electrons of ethene was constructed within an equation-of-motion formalism [10]. In an attempt to improve the model further, we have also determined optimized parameters $1/C_{KL}$ for the directly bonded pairs of atoms. These optimal coefficients turn out to be rather close to $1/R_{KL}$, which suggests that this approximation should be perfectly adequate for the non-bonded atoms. For the remainder of this paper, the energies computed by this model will be identified by the letters SPP, while the energy lowering obtained by allowing $\sigma\sigma^*$ excitations in an MRCI calculation will be called dynamic polarization energy.

It should be pointed out that the validity of this model in no way is dependent on any identification of the charges Q_K with quantities obtained by any quantum-mechanical calculation. They merely serve to elucidate the connection between Eq. (2) and the parameters $1/C_{KL}$, which may be transferable quantities, whereas the coefficients X_{KL} by themselves are not. Also, there is no implication that atomic core polarizabilities are neglected, eventhough this model gives zero SPP energy for an isolated atom. This is simply because the number of sampling points $\boldsymbol{R}_K$, which is $=1$ in this extreme case, is too small to allow proper representation of the perturbing field.

The SPP model potential can easily be incorporated into existing *ab initio* quantum chemistry software. Here, the MOLCAS-1 program package has been used [11]. The one-electron integral generator is modified to store separately nuclear attraction integrals for each atomic centre in the molecule. These matrix elements are then used to construct the one- and two-electron parts of the SPP potential according to Eqs. (6) and (8). There is no need to store separately the two-electron integrals. Instead, they are computed and then immediately added to the normal two-electron integrals for the π-orbitals in the section of the program that transforms these integrals to MO basis.

3. Results

CASSCF calculations were performed on the molecules CH_3^-, C_2H_4 (N, T, and V states), C_3H_5 (allyl radical) and its anion $C_3H_5^-$, and benzene C_6H_6. The calculations were made with and without adding the SPP matrix elements to the integrals. The matrix elements were computed by the capacitance matrix model, as explained above. The parameters were determined to reproduce the dynamic polarization energies obtained from CI calculations on each system except benzene. In each case, two different MRCI calculations were done, one which correlated only the π electrons, and one which also allowed a single electron to be excited out from the σ space. The energies were corrected for unlinked clusters by a multi-reference analogue to the standard Davidson correction [12]. The dynamic polarization energy was then defined as the difference in the Davidson-corrected energies.

In all cases, a standard ANO basis set was used [13], with $3s$- and $2p$-functions for hydrogen, and $6s$-, $5p$-, $2d$-, and $1f$-function for carbon, except for benzene, where the carbon basis set was truncated to $4s3p2d$.

For the hydrocarbons in this study, the capacitance matrix method required four parameters, one each for the carbon and hydrogen atoms, and one each for the carbon-carbon and the carbon-hydrogen bonds. These four parameters were adjusted by non-linear fitting to minimize the sum of the squared errors. There was no indication of secondary minima, and the converged values had a physically reasonable magnitude. The results are presented in Tables 2–5. The root-mean-square error is about 0.13 eV. On the one hand, the errors in the fitted SPP corrections are rather small, on the order of five percent. Furthermore, the obtained ethene excitation energies compare well with experiment, as shown in Table 4. On the other, the remaining errors are certainly not negligible, as shown by the allyl example in Table 5. Also, the small errors in the ethene case could be partly fortuitous, since the experimental V-state excitation energy has not been corrected for the difference between vertical energy and the Franck–Condon maximum, which may amount to as much as 0.3 eV.

Next, using the fitted parameters, the capacitance matrix model was applied to benzene. Separate CASSCF calculations were made for the ^1A_g ground state, and the $^1B_{2u}$, $^1E_{2g}$, and $^1E_{1u}$ states. In this case, we also performed MRCI calculations, using the CASSCF space as reference, and correlating all the π

Table 2. Optimal set of parameters for Capacitance Matrix Model, obtained from least-square fit

Test points K and L	Coefficient $1/C_{KL}$
$K = L =$ a carbon atom	10.0844
$K = L =$ a hydrogen atom	0.899712
$K, L =$ a C–C bond	0.254345
$K, L =$ a C–H bond	0.394953
K, L non-bonded	$1/R_{KL}$
r.m.s. error	0.13 eV

Table 3. σ-π polarization (SPP) energies of various hydrocarbons, computed by MRCI, and approximated by the Capacitance Matrix Method

System	MRCI[a]	SPP[b]	Error	
CH_3^-	2.087 eV	2.076 eV	−0.011 eV ≈	−0.5%
$C_2H_4(N)$	2.852	2.792	−0.060	−2.1
$C_2H_4(T)$	2.668	2.493	−0.175	−6.6
$C_2H_4(V)$	3.589	3.586	−0.003	−0.1
C_3H_5	4.343	4.221	−0.122	−2.8
$C_3H_5^-$	5.283	5.498	+0.215	+4.1

[a] Reference space is identical to CASSCF space. Double excitations are restricted to allow at most one σ hole

[b] CASSCF with valence π orbitals active, with integrals corrected by SPP matrix elements

Table 4. Ethene vertical excitation energies

State	CASSCF[a]	MRCI[b]	SPP[c]	Exp.
T state	4.34 eV	4.52 eV	4.63 eV	4.6 eV[d]
V state	8.49	7.76	7.70	7.66[e]

[a] Valence π orbitals active

[b] Reference space identical to CASSCF. Double excitations restricted to allow at most a single σ hole

[c] Same CASSCF as in a, but with integrals corrected by SPP matrix elements

[d] D. F. Evans, J. Chem. Soc. II, 1735 (1960)

[e] E. K. Johnson, D. B. Johnston and S. Lipsky, J. Chem. Phys. 70, 3844 (1979)

Table 5. Vertical electron affinity of the allyl radical

CASSCF[a]	MRCI[b]	MRCI[c]	SPP[d]
−0.656 eV	−0.604 eV	+0.336 eV	+0.621 eV

[a] 12 π orbitals active

[b] All π orbitals correlated. Davidson correction included

[c] As in b, but also single σ excitations. Davidson correction included

[d] Same as a, but integrals have been corrected by the SPP matrix elements

Table 6. Vertical excitation energies of benzene

	CASSCF[a]	+SPP[b]	MRCI[c]	+SPP[d]	CCI[e]	Exp
$^1B_{2u}$	4.98 eV	5.30 eV	5.01 eV	5.31 eV	5.6 eV	5.0 eV
$^1B_{1u}$	7.92	7.39	7.26	6.99	6.8	6.3
$^1E_{2g}$	8.21	8.51	8.07	8.40	8.1	7.8
$^1E_{1u}$	9.38	8.15	8.14	7.67	7.4	7.0

[a] 12 π orbitals active

[b] Same as a, but with corrected integrals

[c] Reference space identical to CASSCF space, only π correlated

[d] Same as c, but with corrected integrals

[e] From J. M. O. Matos, B. O. Roos, and P.-Å. Malmqvist, J. Chem. Phys. 86, 1458 (1987)

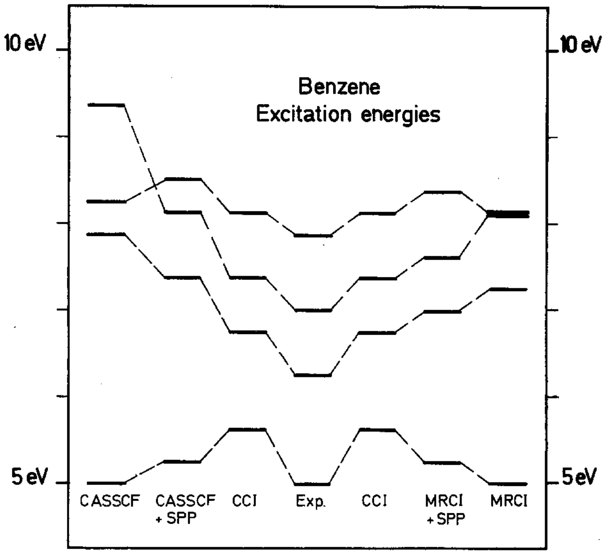

Fig. 1. Calculated and experimental excitation energies of benzene. The CCI results [8] have been included twice, to facilitate comparison with CASSCF as well as MRCI energies

electrons, but no σ. The results are summarized in Table 6, and Fig. 1. From the figure, one can see at a glance that correlation of only π orbitals gives reasonable excitation energies for the two valence states $^1B_{2u}$ and $^1E_{2g}$, but a much too high energy for the ionic states $^1B_{1u}$ and $^1E_{1u}$. Allowing dynamic correlation by inclusion of the extravalence π orbitals by MRCI improves the situation somewhat, but the two ionic states are still about one eV too high. Inclusion of SPP gives the correct order of the excitation energies, but they are now all a bit too high. Evidently, the excited states are treated in a much more balanced way by inclusion of SPP, but the ground state has been stabilized too much, or the excited states too little. An insufficient stabilization, judged from *experimental data*, is of course an expected outcome: The parametrization was made to reproduce the result of including single σ excitations, in order to ensure that the model described a pure dynamic polarization effect. It seems natural that exclusion of double σ excitations gives a too stiff σ skeleton. On the other hand, inclusion of such excitations would allow also other correlation effects than the one investigated, and in order not to confuse the issue it is prudent to use the present type of parametrization. In any case, the probable underestimation of the SPP effect does not explain why there would be a difference on the order of half an eV between the ground vs. excited states. It is quite possible that differential dynamic σ correlation can be significant also. This issue can probably be resolved without having to perform extremely large MRCI calculations, since the contribution of various correlation effects can now be estimated by second order Møller–Plesset perturbation theory using a CASSCF unperturbed wave function [14]. In fact, a recent study of the excited states of pyrazine along these lines shows a large variation in precisely the contributions accounted for by SPP, while other dynamic correlation effects are almost constant in comparison. A similar study for benzene can probably answer the question, whether the SPP was poorly modelled in this case or whether other correlation effects must be blamed.

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