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AN EXAMINATION OF THE BRUECKNER CONDITION FOR THE SELECTION OF MOLECULAR ORBITALS IN CORRELATED WAVEFUNCTIONS*

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Abstract

The Brueckner condition is analyzed as an approximation to the condition of stability of the total energy with respect to variations in the orbitals. The recently introduced method of self-consistent electron pairs is used to find Brueckner orbitals and it is shown that the Brueckner condition can give a slightly higher energy wavefunction than with Hartree-Fock orbitals, while a slightly lower energy result is obtained when singly substituted configurations are important.

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The many-body theory of Brueckner[1-7] leads to a criterion for selecting a set of molecular orbitals for use in a configuration expansion of a wavefunction. Termed the Brueckner condition, this criterion has the simple form

$$C_i^a = 0 \tag{1}$$

where C_i^a is the expansion coefficient of the configuration ψ_i^a formed by substituting the i^{th} occupied orbital with the a^{th} virtual or external orbital in some reference configuration ψ_o. However, as Nesbet[8] has carefully demonstrated, the Brueckner condition is not identical with the condition for minimization of the energy of the wavefunction by variation of the orbitals. Nesbet's conclusion seems to be that the usefulness of (1) may need to be decided empirically, but there has been no abundance of molecular calculations where the Brueckner condition was fully satisfied. The recently developed theory of self-consistent electron pairs[9-10] (SCEP) due to Meyer affords an opportunity to examine the Brueckner condition since Brueckner orbitals which satisfy (1) are easily determined with this method.

For a given wavefunction ψ the condition for minimization of the energy is that the change in energy with first order variations in the wavefunction is zero. Thus, the condition which determines ψ is

$$\langle \psi' | H - E | \psi \rangle = 0 \tag{2}$$

where ψ' is any wavefunction within the configuration space. This results from defining an incremental change in the wavefunction using a parameter, ε

$$\delta\psi = \psi' \, \delta\varepsilon \tag{3}$$

and setting $dE/d\varepsilon$ equal to zero. If ψ is a configuration expansion of the wavefunction, the variations $\delta\psi$ can be variations in the expansion coefficients or variations in the orbitals. Assuming the expansion coefficients are optimally determined, the following variations can be made in the orbitals.

$$\delta\psi: \qquad \delta\phi_i = \phi_a \, \delta\varepsilon \quad \text{and} \quad \delta\phi_a = -\phi_i \, \delta\varepsilon \tag{4}$$

That is, in each configuration ψ_L in ψ we have

$$\delta\psi_L = \psi_L^{i,a} \, \delta\varepsilon \tag{5}$$

where $\psi_L^{i,a}$ is the configuration formed by replacing the i^{th} orbital in ψ_L with the a^{th} orbital or by replacing the a^{th} with the negative of the i^{th} orbital. If i and a are both occupied in ψ_L then $\psi_L^{i,a}$ may, in fact, represent two configurations;[8] simultaneous replacement of two orbitals can be discarded as a second order variation not used in $dE/d\varepsilon$.

A trivial form of the wavefunction is $\psi = \psi_o$ where (2) and (4) give

$$\langle \psi_i^a | H | \psi_o \rangle = 0 \tag{6}$$

This is just Brillouin's theorem which shows that the Hartree-Fock energy is stable with respect to first order variations in the orbitals.[12] Next, consider a wavefunction which includes the reference configuration and all doubly substituted configurations (ij → ab).

$$\psi = C_o\psi_o + \sum_{ij} \sum_{ab} C_{ij}^{ab} \, \psi_{ij}^{ab} = C_o\psi_o + \sum_L C_L\psi_L \tag{7}$$

$$\langle C_o\psi_i^a + \sum_L C_L\psi_L^{i,a} | H - E | \psi \rangle = 0 \tag{8}$$

The condition given by (8) is the condition for the best choice of orbitals in the expansion and if the ψ_L are not limited to double substitutions, (8) is general for any expansion. Brueckner's condition is that the singly substituted configurations will have a zero Hamiltonian matrix element with the total wavefunction and thus, will have a zero expansion coefficient, i.e.(1). This implies approximating the summation term in (8) as zero. As Nesbet[8] has indicated, this might serve as a reasonable approximation since many of the neglected terms depend quadratically on the C_L coefficients.

If (8) is separated and terms which depend quadratically on the C_L coefficients (but not C_o which is approximately 1 when ψ_o dominates) are neglected the following is obtained.

$$\langle \psi_i^a | H - E | \psi - C_{ii}^{aa}\psi_o \rangle - \sum_{b\neq a} C_{ii}^{ab} \langle \psi_i^b | H - E | \psi_o \rangle - \sum_{j\neq i} \sum_{b} C_{ij}^{ab} \langle \psi_j^b | H - E | \psi_o \rangle = 0 \qquad (9)$$

Therefore, the energy stability condition to first order in the C_L's shows that the singles do not vanish independently. If it were assumed that the orbitals which satisfy (9) were close to the Hartree-Fock orbitals, then the Brueckner condition should be sufficient for selecting orbitals.

Now, let us consider in place of (7) a wavefunction which explicitly includes singles:

$$\psi = C_o\psi_o + \sum_{ia} C_i^a \psi_i^a + \sum_{ij} \sum_{ab} C_{ij}^{ab} \psi_{ij}^{ab} \qquad (10)$$

Again, neglecting quadratic C_L terms gives the approximate condition for the minimum energy choice of orbitals.

$$\langle \psi_i^a | H - E | \psi - C_{ii}^{aa}\psi_o \rangle - \sum_{b\neq a} C_{ii}^{ab} \langle \psi_i^b | H - E | \psi_o \rangle - \sum_{j\neq i} \sum_{b} C_{ij}^{ab} \langle \psi_j^b | H - E | \psi_o \rangle$$
$$- C_i^a \langle \psi_o | H-E | \psi_o \rangle + \sum_{jb} C_j^b \langle \psi_{ij}^{ab} | H - E | \psi_o \rangle = 0 \qquad (11)$$

The term $\langle \psi_o | H - E | \psi_o \rangle$ is the correlation energy and is typically non-negligible. Hence, the Brueckner condition is a somewhat poorer approximation for a wavefunction including singles than one including only doubles. Table I gives results comparing Brueckner and Hartree-Fock orbitals for methylene and it is seen that the Brueckner condition does yield a lower energy for a wavefunction like (7) but is slightly worse than using Hartree-Fock orbitals with the wavefunction of (10). The difference in total energies is small, since it is well known[13] that configuration interaction including all single and double substitutions yields essentially the same energy using SCF or natural orbitals (or similarly Brueckner orbitals). In calculations on H_2O, CH_2 with several basis sets, and acetylene, the Brueckner orbital result was always higher than the energy of the singles and doubles wavefunction using Hartree-Fock orbitals; exceptions were LiH[10] and BH.

Larsson and Smith[14] have described Brueckner orbitals as best-overlap orbitals in the sense that they give the best overlap of a one-configuration approximation of the wavefunction with the true wavefunction. This would suggest that a Brueckner orbital configuration expansion may be appropriate for the determination of properties just as with natural orbitals. A very interesting comparison of configuration expansions with different orbital sets has been given recently by Shavitt, Rosenberg and Palalikit.[15] They showed that convergence of one-electron properties is much better with natural orbitals than Hartree-Fock orbitals, among others, and the natural orbitals used were apparently close to Brueckner orbitals, since the singles contribution to the wavefunction was found to be small (ref. 15, Table VI). When a complete singles and doubles expansion is used,however, it may not be as essential to use natural or Brueckner orbitals.

Since the Brueckner condition produced a higher energy singles and doubles wavefunction than with Hartree-Fock orbitals, it was of interest to determine if a lower energy result could be obtained and so, an experiment of sorts was performed. Noting the direction of the energy change when the singles were made unimportant suggests performing the first order perturbation improvement in the orbitals,[9-10] used to achieve the Brueckner result, in roughly the opposite sense (opposite sign corrections to the occupied orbitals). This was tested on H_2O as shown in Table II and the lowest energy was obtained with several such iterations during which the singles became substantially important.

The dipole moment was not greatly changed, though whether the change is better or worse is an empirical decision at this point. The increased importance of the singles could be important in expansions larger than those inlcuding just singles and doubles, since a large part of the remaining correlation energy might be obtained by including triples, the highest substitutions which would have non-zero interaction with the singles, without necessarily having to include the quadruples which interact with the doubles.

The Brueckner condition is an approximation to the energy stability condition, not even correct to first order in the C_L's. However, the conditions correct to first order, given by (9) or (11), are difficult to implement. The coupling of the conditions on the individual singly substituted configurations in (9) and (11) points toward the possibility that the singles are not unimportant in the lowest energy wavefunction, opposite to the Brueckner condition, and this seems to be supported by the H_2O test calculation.

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Table I. Brueckner Orbitals for Methylene. The calculations done with SCEP used a basis set of 42 functions as in ref. 10. Huzinaga's[16] (10s 6p) carbon basis and (5s) hydrogen basis were contracted using Dunning's[17] scheme to (6s 4p) and (3s), respectively. The hydrogen scale factor was 1.49. Hydrogen p functions and carbon d functions were added as in the calculations of Bender <u>et al</u>.[18] The C-H bond length was 1.11 Å and the bond angle was 102.4° and the lowest occupied orbital was frozen to substitution. Energies are in au.

Energy Computed with ψ Including:	Hartree-Fock Orbitals	Brueckner Orbitals
Reference Determinant, ψ_o, Only	-38.892 387	-38.891 365
ψ_o and Double Substitutions Only as in (7)	-39.038 740	-39.039 501
ψ_o and Single and Double Substitutions as in (10)	-39.039 621	-39.039 501

Table II. Orbital Sets in H_2O Wavefunctions. The double-zeta basis set of 14 contracted functions and the molecular geometry were those used by Hosteny *et al.*[19] Energies are in au.

	Energy for Wavefunctions Including:					
	Reference Determinant, ψ_o	ψ_o + Doubles as in (7)	ψ_o + Singles + Doubles as in (10)	$\sum_{ij,ab}\sum {c_{ij}^{ab}}^2$	$\sum_{ia} {c_i^a}^2$	Dipole Moment (Debyes)
SCF	-76.009 256	-	-	-	-	2.684
CI - SCF orbitals[19]	-76.009 256		-76.135 406			
SCEP - SCF orbitals Brueckner iteration 1	-76.009 256	-76.134 592	-76.135 386	0.040 288	0.000 603	2.587
SCEP - Brueckner iteration 2	-76.008 389	-76.135 037	-76.135 056	0.040 636	0.000 011	2.578
SCEP - Brueckner iteration 3	-76.008 430	-76.135 076	-76.135 076	0.040 643	-	2.577
SCEP - Important-singles iteration 2[a]	-76.008 396	-76.132 406	-76.135 611	0.039 874	0.000 812	2.593
SCEP - Important-singles iteration 3[b]	-76.005 405	-76.127 866	-76.135 663	0.039 405	0.001 216	2.599
SCEP - Important-singles iteration 4[b]	-75.999 079	-76.119 658	-76.135 353	0.038 761	0.001 944	2.604

[a] The first iteration where the singles are forced to become important uses the SCF orbitals and thus, is identical with the first Brueckner iteration.

[b] The third iteration where the singles are important gives the lowest energy and since the process is not self-consistent, it eventually diverges to a worse result. Notice, however, that the energy in the fourth

Table II continued.

iteration is about equal to that with SCF orbitals even though the wavefunctions are considerably different. Indeed, this last iteration's result would probably give at least as low an energy as with the SCF orbitals, if the effect of the singles on the doubles were included. This effect -- allowing the doubles to relax when the singles are included in the wavefunction -- is neglected in SCEP which accounts for the difference in the CI and SCEP energies when using SCF orbitals. The effect is typically small when using SCF orbitals[10] but when the orbitals are such that the singles are more important, the effect on the total energy should be somewhat greater.

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