# Many-Body Perturbation-Theory Calculations for Excited Molecular States

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The folded-diagram procedure of Brandow, suitable for many-body perturbation-theory calculations when unperturbed functions are degenerate, is applied to the four lowest excited $\Sigma^+$ states of $H_2$ at $R = 1.4$ bohr. Calculating energies up to third order (inclusive) and estimating higher-order corrections, an agreement of 1 kcal/mole is obtained with the accurate results of Kolos and Wolniewicz.

The many-body perturbation theory (MBPT) of Brueckner[1] and Goldstone[2] was first applied to atomic systems by Kelly.[3] The method has proved very useful, and numerous calculations of correlation energies and other atomic properties have been carried out by Kelly[4] and others.[5] A more recent development is the application to molecular systems.[6-8] The expansion of the perturbation series by the linked Goldstone diagrams is applicable only if the unperturbed function can be represented by a single Slater determinant. This is the case for the ground state of many atoms and most molecules, as well as for some excited states, such as the Ne 1*s*- and 2*s*-hole states investigated by Chase, Kelly, and Kohler.[9] Most excited states fall, however, outside the scope of this method, and because of the great interest in such states it would be highly desirable to find a MBPT method capable of handling degeneracies. This problem was first solved by Bloch and Horowitz[10] using Brillouin-Wigner perturbation theory for particles outside closed shells. Brandow[11] rederived the Bloch-Horowitz results and cast them in a "completely linked" form, and similar methods, differing in derivation and diagram representation, have appeared since.[12,13] The present work uses the diagram expansion and representation introduced by Brandow.[11]

The rules for drawing and calculating the energy diagrams will not be described in detail, as they may be found in the original papers.[10-13] Some differences between Goldstone and Brandow energy diagrams shall, however, be noted. In the Brandow formulation, unperturbed one-electron orbitals fall into three classes: (a) core orbitals, occupied in all of the Slater determinants which form the unperturbed degenerate space; (b) valence orbitals, occupied in some of these determinants; and (c), intermediate (or particle) orbitals, unoccupied. Unlike the Goldstone energy diagrams, the Brandow diagrams are open (see Figs. 1 and 2), with the incoming (and outgoing) lines representing a particular occupancy of the valence shell, corresponding to one of the unperturbed degenerate Slater determinants. The internal lines may be hole lines (summed over core orbitals), particle lines (summed over intermediate orbitals and, with certain restrictions,[11] over valence orbitals), and folded lines (summed over valence orbitals). All linked diagrams with the incoming state *i* and outgoing state *j* are combined to obtain the *ij* element of the secular matrix, which is then diagonalized to yield the perturbative energy correction as well as the projection of the perturbed functions upon the unperturbed degenerate space (i.e., the linear combination of the degenerate unperturbed states reached from the perturbed function upon turning the perturbation off adiabatically).[11,13]

The Brandow technique is applied in this paper to the four lowest excited $\Sigma^+$ states of the hydrogen molecule at $R = 1.4$ bohr. The unperturbed functions of these states may be written as

$$\psi_0 = 2^{-1/2} A(a\alpha b\beta \pm b\alpha a\beta), \qquad (1)$$

where the plus and minus signs apply to singlet and triplet states, respectively, *a* is the $1\sigma_g$ or-

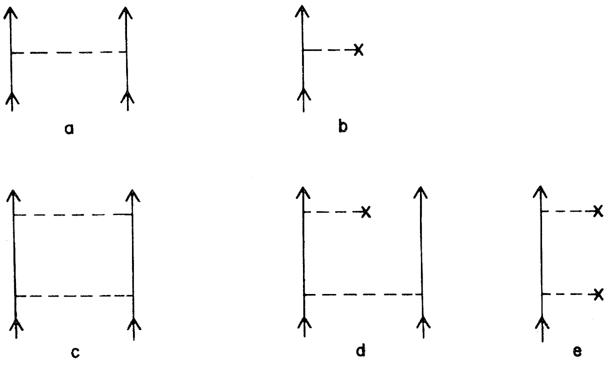

FIG. 1. First- and second-order diagrams. A cross denotes the one-electron part of the perturbation. Diagram (d) can be inverted.

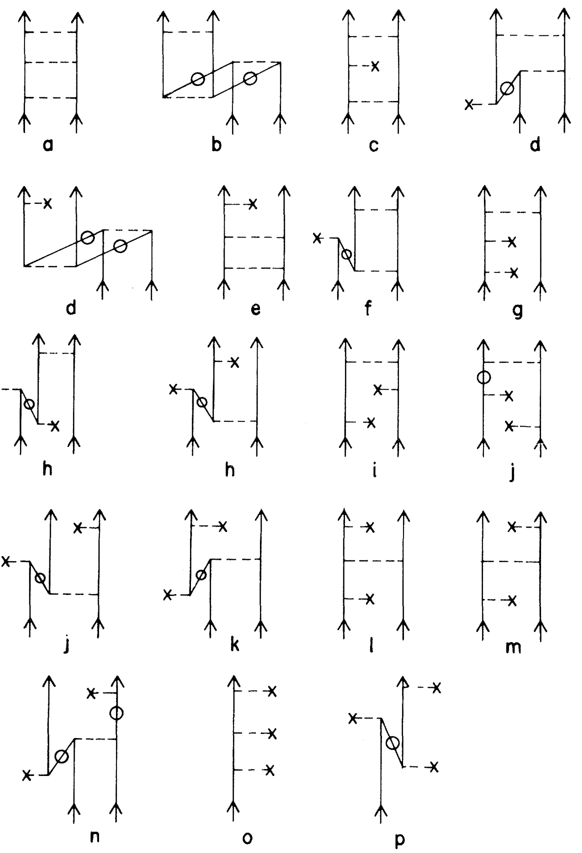

FIG. 2. Third-order diagrams. A circle denotes a folded line. Different diagrams which are numerically identical are given the same name. Diagrams (e), (g), and (i) can be inverted.

TABLE I. Electronic energies (in a.u.) of $\Sigma^+$ excited states in $H_2$; $R = 1.4$ bohr.

| Order | $B\,^1\Sigma_u^+$ | $b\,^3\Sigma_u^+$ | $B\,^1\Sigma_g^+$ | $a\,^3\Sigma_g^+$ |
|---|---|---|---|---|
| | | Hartree potential | | |
| 0 | − 0.75543 | − 0.75543 | − 0.72447 | − 0.72447 |
| 1 | − 0.60932 | − 0.70781 | − 0.64152 | − 0.67561 |
| 2 | − 0.07323 | − 0.04343 | − 0.05489 | − 0.03462 |
| 3 | 0.02146 | 0.01120 | 0.02228 | 0.01000 |
| Higher[a] | − 0.00486 | − 0.00230 | − 0.00643 | − 0.00224 |
| | | Bare-nucleus potential | | |
| 0 | − 1.89621 | − 1.89621 | − 1.67881 | − 1.67881 |
| 1 | 0.67093 | 0.43991 | 0.34867 | 0.28762 |
| 2 | − 0.18374 | − 0.03820 | − 0.08059 | − 0.03460 |
| 3 | − 0.01124 | − 0.00220 | 0.00956 | 0.00024 |
| Higher[a] | − 0.00073 | − 0.00013 | − 0.00101 | 0.00000 |

[a] Estimated; see text.

bital, and $b$ is the $2\sigma_g$ orbital for *gerade* states and the $1\sigma_u$ orbital for *ungerade* states. Two simplifications to the general Brandow formulation apply here. First, there are no core orbitals, and diagrams with internal hole lines need not be taken into account. Second, while the degenerate space for each of these states is two-dimensional, the linear combination corresponding to each state is of course known [Eq. (1)] and no secular equation has to be solved. It is easily shown that the perturbation energy is given by

$$\Delta E = \langle a\alpha b\beta|W|a\alpha b\beta\rangle \pm \langle a\alpha b\beta|W|b\alpha a\beta\rangle, \qquad (2)$$

where the orbitals and signs are the same as in Eq. (1), and the operator $W$ represents all Brandow diagrams, with incoming orbitals written to its left and outgoing orbitals to its right. The triplet states may of course be also described by a single determinant $A(a\alpha b\alpha)$ and treated by the usual Goldstone expansion. An order-by-order comparison of the two calculations may serve as a check on the enumeration and evaluation of the diagrams.

The basis set used in this work is the $10s5p1d$ Gaussian set employed by Schulman and Kaufman[8] for the ground state of $H_2$. Other recent work[14,15] also indicates that basis sets consisting of a finite number of bound-type orbitals are applicable to MBPT atomic and molecular calculations. We tried a limited amount of exponent variation, but no significant changes in diagram values were obtained. Two zero-order potentials were used to obtain the unperturbed orbitals. One set of orbitals was calculated in the field of the nuclei and one $1\sigma_g$ electron, corresponding to the Hartree potential[8] or Kelly's[16] $V^{N-1}$. Another set of calculations was performed with the bare-nucleus potential.[17] The same orbitals gave good results for the molecular ground state.[8,18] Being able to handle several molecular states with the same set of orbitals is highly desirable, both because of saving in computational effort and the relative ease of calculating transition probabilities.

Diagrams contributing to the electronic energy in the first and second orders are collected in Fig. 1, and third-order diagrams are shown in Fig. 2. The one-electron potential added to the kinetic energy and nuclear attraction terms to form the zero-order Hamiltonian appears in the perturbation operator with a minus sign,[3] and is denoted by a cross. The dashed horizontal lines represent the electron repulsion operator. The cross interaction vanishes for the bare-nucleus potential, and diagrams including it do not appear in this case.

TABLE II. Total electronic energy (in a.u.).

| | Hartree potential | Bare-nucleus potential | Accurate[a] |
|---|---|---|---|
| $B\,{}^1\Sigma_u^+$ | $-1.4214$ | $-1.4210$ | $-1.4200$ |
| $b\,{}^3\Sigma_u^+$ | $-1.4978$ | $-1.4968$ | $-1.4984$ |
| $E\,{}^1\Sigma_g^+$ | $-1.4050$ | $-1.4022$ | $-1.4062$[b] |
| $a\,{}^3\Sigma_g^+$ | $-1.4269$ | $-1.4256$ | $-1.4279$ |

[a] Ref. 19.
[b] Interpolated.

The order-by-order contributions to the electronic energy, up to third order, are presented in Table I. Higher-order corrections are estimated by assuming that contributions of consecutive orders, beginning with the second, form a geometric progression. Results obtained for the triplet states using the Goldstone diagrams agree with the values in Table I to the number of figures given there.

The errors in our final energy values (Table II) are of two kinds. The expansion error, due to the incompleteness of the basis set used, may be estimated by comparing our bare-nucleus results with those of Goodisman,[17] obtained with extensive sets of James-Coolidge-type functions. Agreement is better than $10^{-3}$ a.u., and similar convergence with respect to the basis set is expected for the Hartree potential. The second, more serious error results from the approximate inclusion of the higher-order corrections. We estimate this error as $(1-2)\times 10^{-3}$ a.u. Comparison of the calculated electronic energy of the four excied $\Sigma^+$ states with the accurate values of Ref. 19 (see Table II) shows agreement to about 1 kcal/mole, within the error limits quoted. The only exception is the bare-nucleus calculation of the ${}^1\Sigma_g^+$ state, where the somewhat larger error can probably be ascribed to the proximity of another ${}^1\Sigma_g^+$ level, with $1\sigma_u^2$ configuration. Brandow's method is flexible enough to handle quasidegeneracy[11] by counting $1\sigma_u$ as a valence orbital, but this complicates the calculation somewhat and has not been done here. The $1\sigma_u$ orbitals will have to be included in the valence set at larger internuclear separation, where the two ${}^1\Sigma_g^+$ states approach and eventually cross. The agreement between results obtained with the two potentials is remarkably good, considering the large differences between zero-order energies.

In conclusion, we have shown that Brandow's method of folded diagrams is applicable to excited, degenerate molecular states. Another possible application is in cases of quasidegeneracy. Further investigations using this method are in progress, and it may be reasonably expected that it should prove as useful to excited-state calculations as the use of Goldstone diagrams did for molecular ground states.

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