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Self-consistent-field – Hartree–Fock method with finite nuclear mass corrections

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Abstract. We have upgraded a Self-consistent-field – Hartree–Fock routine to include a finite nuclear mass correction for molecules developed in our laboratory. The new routine can handle isotopomers without calculating any nuclear kinetic energy matrix element. Tests on H_2, LiH, HF, F_2, and H_2O isotopomers indicate the equivalence of our correction to the standard diagonal adiabatic correction. A further original application to C_2H_6 illustrates the usefulness of the method for polyatomic molecules. The resulting molecular orbitals carry the nuclear mass signature, exemplified with Koopmans' ionization potentials.

Keywords: Isotopomers – Isotope effect – Adiabatic approximation – Born–Oppenheimer aproximation – Finite nuclear mass

1 Introduction

Most ab initio molecular calculations resort to the Born–Oppenheimer (BO) approximation. On this level, the only point where finite nuclear mass effects (the isotope problem) are concerned is in the solution of the (quantal or classical) nuclear equations of motion. The increasing experimental accuracy, however, demands the inclusion of finite nuclear mass effects in the solution of the electronic problem, i.e., in the generation of potential-energy surfaces (PES). When the problem involves isotopes of the hydrogen atom, the nuclear mass corrections are even more important than the relativistic ones.

One way to include these effects in the PES is through the diagonal (or adiabatic) BO corrections (DBOC), and a self-consistent-field (SCF) methodology for this has been developed by Handy et al. [1]. In this method, the DBOC is obtained by averaging, with the SCF–BO wavefunction, the nuclear kinetic energy operator in the laboratory frame, instead of the body-fixed molecular frame, a procedure that avoids mixing of electronic and nuclear coordinates (the mass polarization terms). Kutzelnigg [2] has proved the theoretical correctness of this procedure and Cencek and Kutzelnigg [3] checked its accuracy for H_2 with a correlated wavefunction. Handy and coworkers [1, 4] reported test calculations of SCF–DBOC for some small molecules in their equilibrium geometries. Dinelli et al. [5] and Polyansky et al. [6] explored the method to improve theoretical predictions for the transition frequencies of H_3^+. More recent applications are those by Tarczay and coworkers in studies of the barriers to linearity of H_2O [7] and H_2S [8].

In spite of these advances, relative to more difficult calculations that use internal coordinates [9], there are remaining difficulties in the calculation of matrix elements of nuclear kinetic energy operators for larger systems, which seems to be an obstacle to the generalized application of this method. Besides that, in its very conception, DBOC does not modify the wavefunction, i.e., the calculation of molecular properties is not affected by the nuclear motion corrections.

In this paper, we introduce a new molecular orbital – linear combination of atomic orbitals (MO–LCAO) method on the Hartree–Fock (HF) level that is able to handle finite nuclear mass effects and present some new features. First, it explores the machinery of standard SCF–BO computer programs, with no need of calculation of new matrix elements, meaning no extra computational burden and no other limitations than those common to standard SCF–HF calculations. Second, it imparts to the MOs the signature of the nuclear masses, affecting the calculation of molecular properties.

As a consequence of this last point, we are faced with a question that concerns the fundamentals of MO theory, namely the geometrical symmetry properties of

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the MOs generated by the new approach. The very existence of this kind of symmetry is usually questioned as one works beyond the BO approximation. In a previous work on the symmetry properties of the MOs of HD^+ [10] we found that, as we include the nuclear mass effects, the MOs present an overall reduction of the point group symmetries, from $D_{\infty h}$ to $C_{\infty v}$, but a correlation diagram can be generated, in which the new symmetries are preserved and the noncrossing rule is mantained as well. A generalization of these conclusions to polyatomic molecules is still missing, and we thus postpone the general study of isotope symmetry-breaking to a future publication. In consequence, we limit our applications here to systems in which the nuclear mass effects do not yield symmetry-breaking. For instance, we calculate D_2O, but not HDO.

Methodology and tests

Based on the realization that the adiabatic correction is much like a reduced mass effect [4], a finite nuclear mass correction (FNMC) for molecules has been developed in our laboratory [11, 12]. It was tested in calculations of an one-electron diatomic molecule with a single MO [11] and a two-electron diatomic molecule with a valence bond wavefunction [12], and was shown to be quite close to accurate DBOC calculations. In our approach, however, a fundamental difference from DBOC is that we keep the spirit of variational adiabatic calculations, in which the electronic wavefunctions are approximate eigenfunctions of the total Hamiltonian, instead of the BO one. This widens the applicability of FNMC to exotic molecular systems with very light nuclei [13], a case in which the BO–based methods are useless. Furthermore, the outcoming wavefunction carries itself the signature of the nuclear masses and, consequently, of eventual isotope asymmetries [10].

For simple one- and two-electron molecules [11, 12, 14], our approach was based on the construction of an effective BO Hamiltonian, in which the electron mass is scaled (becoming a function of the internuclear distance) so that both the united atom (UA) and separated atom (SA) asymptotic limits are correctly obtained (except for possible very small mass polarization terms for different electrons). This is granted by the procedure of optimizing the atomic orbitals so that the total energy is minimized; this was first introduced by Rost and Briggs [15]. By postulating, for finite nuclear distances, an atomic form for the electron reduced mass, we arrived at the FNMC (Eq. 9 of Ref. [12], for example). Although this effective BO Hamiltonian formalism is not feasible for larger molecules, its outcome becomes very simple to generalize: “whenever an electron occupies an AO, we must add to its kinetic energy an *atomic* mass polarization correction”. Explicitly, for a MO–LCAO wavefunction, consider the BO total energy in terms of a set of AOs, or basis functions, $\{\phi_{\mu A}\}$, where A is the nucleus where the orbital is centered and μ stands for all other AO features. To each electronic kinetic energy matrix element of the kind $T_{\mu\nu AB} = \left\langle \phi_{\mu A} \middle| -\frac{\nabla^2}{2} \middle| \phi_{\nu B} \right\rangle$ we add the correction

$$Q_{\mu\nu A} = \begin{cases} \frac{T_{\mu\nu AB}}{M_A} & \text{if } A = B \\ 0 & \text{if } A \neq B \end{cases} , \tag{1}$$

where M_A is the mass of nucleus A relative to the electron mass $M_e = 1$ au. In other words, the individual corrections apply just to single-center matrix elements. The mass-dependent total energy, symbolized by $E = E_{BO} + Q$ (where Q, the total correction, also depends on the squares of the linear coefficients) is then minimized. This prescription becomes exact for one-electron atoms, nearly exact for many-electron atoms, and presented very good results for one- and two–electron diatomic molecules with different wavefunctions [10, 11, 12, 13, 14]. It is important to note that the joint procedure of mass scaling of the electronic BO Hamiltonian and variational optimization of the AOs, that leads to proper UA and SA limits, allows us to obtain not only the common molecular diagonal mass polarization correction (that accounts just for the correct UA limit), but also a substantial amount of the internal nuclear kinetic energy correction. Further details about this point are in Ref. [11, 12].

Here we report an upgrade of a SCF–HF routine to include the FNMC. As stated previously [1, 4], the SCF level is appropriate to perform adiabatic corrections to PES. The original routine is one developed (and kindly granted to us) by Rico et al. [16] in which all two-center integrals are evaluated with Slater-type orbitals (STOs). Although not a sine qua non condition, this is very convenient for our purposes. In fact, the correction of a typical ten-electron molecule affects the third decimal digit of the energy (atomic units), i.e., the HF energy must be converged at least in this place, in order for the correction to be meaningful, which is much more easily attained with STOs than with the more usual Gaussian-type orbitals.

In the closed-shell restricted HF–MO–LCAO approximation, keeping the same notation as earlier, we write the HF energy as

$$E = \frac{\langle \Phi | \mathbf{H}_{BO} + \mathbf{Q} | \Phi \rangle}{\langle \Phi | \Phi \rangle} , \tag{2}$$

where Φ is a Slater determinant built with AOs, and the notation for the operator $\mathbf{Q}$ is symbolic, meaning just that the previous prescription is followed. Minimizing E relative to the MOs leads us to redefine the usual Fock matrix elements as

$$F_{\mu\nu}^{\text{fnmc}} = F_{\mu\nu} + Q_{\mu\nu A} \tag{3}$$

and the HF energy as

$$E^{\text{fnmc}} = \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu} (h_{\mu\nu} + F_{\mu\nu}^{\text{fnmc}}) , \tag{4}$$

where $h_{\mu\nu}$ and $F_{\mu\nu}$ are, respectively, the standard core and Fock matrices, $P_{\mu\nu}$ is the density matrix and the corrections $Q_{\mu\nu A}$ are those defined in Eq. (1). Thus, the subscript A in the second term of Eq. (3) means that the corrections are added just to single-center matrix elements. Except for these changes, the applications follow the lines of standard SCF–MO–LCAO calculations.

Computations of a series of closed-shell diatomic and triatomic molecules, with 2–18 electrons, were made in order to compare FNMC with DBOC. An illustrative original calculation with an eight-atom molecule, C_2H_6, completes our examples. In the calculations, neutron and proton masses are taken as 1836.1527 au.

The only system for which exact DBOCs are available is H_2 [17], amounting to 114.591 cm^{-1} (1 hartree $=$ 219474, 631 cm^{-1}) at the equilibrium distance, $R = 1.4$ au. The MC–SCF result for DBOC, from Ref. 4, is 101 cm^{-1}. As a general rule, SCF calculations make part of the correction, viz. the mass polarization terms for different electrons, vanish. For H_2 this term amounts to about 5.2% of the total correction [17], which explains part of the difference reported in Ref. [4]. Our HF–SCF correction, for a large basis set, amounts to 85 cm^{-1}, a disappointing but deceptive result that we attribute to the bad HF description of H_2 and not to the approach itself. In fact, with a valence bond wavefunction we have obtained much better agreement [12].

On the other hand, tests with LiH, HF, F_2, H_2O, and D_2O have yielded stimulating results. The results, shown in Table 1, correspond to basis sets that reproduce the HF limit energy with an appropriate number of digits. The equilibrium geometries are reoptimized, but differ very little from the BO ones, for equal basis sets. We observed similar behavior with DBOC [1] concerning changes in the basis sets, i.e., FNMC becomes lower and converges as the basis set is improved.

The FNMC for LiH is still bellow, but much closer to, the corresponding DBOC, as compared to the H_2 case. On the other hand, for the other molecules, FNMCs becomes systematically 6–7% larger than DBOC. This turns to be a very convenient feature in view of the vanishing of the mass polarization term in any SCF calculation. We are thus led to speculate that our approach overestimates the correction by an amount that, with good approximation, compensates the absence of this term. This feature is potentialy able to make SCF–FNMC more accurate than SCF–DBOC but, unfortunately, this could not be checked in view of our bad results for H_2. A last test calculation with HCl advances a problem that did not appear in another 18-electron system (F_2). The mass of the Cl nuclei is large enough to deteriorate the corrections for individual electrons, so that the final FNMC is a sum of many less accurate small terms, and is also less accurate. To account for this problem we will probably need to work with saturated basis sets. Anyway, the adiabatic corrections to heavy-nuclei molecules become relatively less important and much lower than the relativistic ones.

Table 1. Comparison between finite nuclear mass correction (*FNMC*) (this work) and diagonal Born–Oppenhemer corrections (*DBOC*), as well as between Koopmans' ionization potentials from BO calculations (*IP–BO*) and from this work (*IP*)

Molecule	DBOC (cm^{-1})	FNMC (cm^{-1})	IP–BO (au)	IP (au)
H_2	101[a]/114.6[b]	85.2	0.596868	0.596752
LiH	189.55[c]	180.2	0.301159	0.301168
HF	605.9[a]	642.5	0.652318	0.652285
H_2O	595[d]	640.4	0.508461	0.508225
D_2O	554[d]	597.1	0.508461	0.508345
F_2	1133.8[a]	1216.7	0.646030	0.645988
C_2H_6	–	1075	0.488486	0.488059

[a] Ref. [4]
[b] Ref. [17]
[c] Ref. [19]
[d] Ref. [1]

The last system that we consider is C_2H_6, with the corresponding data shown also in Table 1. We have not found any previous calculation of the adiabatic correction to this or any other molecule with nuclearity larger than 5 (the largest nuclearity we have detected is for a few-electron system, H_5^+ [1]) so we include this calculation as illustrative of the new facility allowed by our method. The calculation was done with a staggered optimized conformation. The effects of the FNMCs on the internal rotation barrier will be the subject of further detailed investigation.

The isotope effect on the MOs and final remarks

Though the MOs depend on the nuclear masses, the HF level is not accurate enough to obtain small isotope effects like the dipole moment of HD [18]. Our calculations of this quantity, despite giving a nonzero value and the correct order of magnitude, did not converge to a reliable value. This feature must be corrected by a higher-level electronic structure calculation (valence bond, multiconfigurational SCF, etc.).

Here we illustrate the effect of FNMCs on the orbital properties with the Koopmans' ionization potentials (IP) for the various molecules considered Table 1. The difference between the predicted IPs for water and its isotopomer D_2O is particularly illustrative, showing that a little more energy is needed to pull an electron out from D_2O than from H_2O. Another remark is that, though the large difference from Koopmans' IPs to experimental values is due to the lack of correlation, our values point correctly to the experimental results, which means smaller IPs.

Since all the methodological problems reported here are ascribed not to the method itself, but to the HF level of approximation, it seems natural to go to higher levels of configuration interaction to improve its capability. This is presently being considered in our group.

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