Original Research Article

Ab-initio quantum chemistry through computer algebra

Abstract

In this article, we demonstrate the first-principles computation of quantum chemistry through symbolic computation, using computational algebraic geometry. We have developed a Python program that generates symbolic formulas of one- and two-electron integrals. The approximations of those integrals by multivariate polynomials yield the set of equations required by quantum chemistry. We solve these equations in hybrid ways where numeric and symbolic computations are intertwined. We discuss the possibility of the extension of our scheme to treat the models beyond the Born-Oppenheimer approximation.

Keywords: Quantum Mechanics; Quantum Chemistry; Computational Algebraic Geometry; Gröbner basis; Symbolic Computation;

2020 Mathematics Subject Classification: 81-08; 14Q99

1 Introduction

In [10], A. Kikuchi presented an example of the first principles of electronic structure computation through *algebraic* approach, wherein a contemporary technique of computational algebraic geometry is adopted. The author of that article prepared the analytic energy functional of one hydrogen molecule and approximate it by a polynomial. Then he composed a set of polynomial equations which give the minima of the energy functional (through the symbolic differentiation) and was successful in solving it using the Gröbner basis technique. As for the construction of one or two-electron integrals, he used the Slater-Type Orbitals (STO) for atomic bases – even if it is not the standard way of today's quantum chemistry. In the appendix of the article, he presented the analytic expression of necessary integrals; some of them are quite complicated because of the mathematical nature of analytical integration involving STO. It is a very technical and tough problem how to do analytical integration of two-electronic integrals with STO, and it has not yet been settled. For this reason, we should use

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the conventional way of quantum chemistry, employing Gaussian Type Orbitals (GTO). To unwind this deal and make a fresh start all over again, in the present article, we give another example of molecular electronic structure computation, for which electronic integrals are analytically computed by GTO. The formulas presented below shall serve the readers as a kind of benchmark test for the algebraic method proposed in [10]. In the following, we describe the problem setting and report the result of symbolic and numeric computations.

We use higher algebra in this article. The essence of mathematics required hereafter is reviewed in [12], [13], and [11].

If you would like to get rigorous theories, you should consult the following references.

- Commutative algebra: Eisenbud [6]
- Gröbner basis: Cox et al.[3, 2]; Ene and Herzog; [7]
- Primary ideal decomposition and triangulation of Gröbner basis: Gianni et al.[9], Mollrer [16];Lazard[15]
- Solving systems of polynomial equations through linear algebra: Sottile[17]
  Computational algebraic geometry: Decker [5]

2 Model Description

We take $\mathrm{HeH+}$ as an example and employ minimal STO-3G bases to describe the electronic structure. Concerning this matter, an out-fashioned FORTRAN program is attached to [18], and it is available on the internet. We rewrite it into a Python program for numerical and symbolic computations to prepare the formula of the total energy.

Now we give a brief account of the program.

We assume a heteronuclear diatomic molecule, where the nuclei A and B are located at the points R_A and R_B; the nuclear charges are given by Z_A and Z_B: and the interatomic distance is $R = |R_A - R_B|$. We use STO-NG bases with N=1,2,3, located at the nuclei A and B. We denote them by $\phi_i(r, R_i)$ with $i = 1, 2$ and $R_i = R_A, R_B$.

The RHF wavefunction is defined by

$$\psi(r) = x \cdot \phi_1(r, R_A) + y \cdot \phi_2(r, R_B). \tag{2.1}$$

The UHF wavefunctions are defined by

$$\psi_\alpha(r) = x \cdot \phi_1(r, R_A) + y \cdot \phi_2(r, R_B), \tag{2.2}$$

and

$$\psi_\beta(r) = u \cdot \phi_1(r, R_A) + v \cdot \phi_2(r, R_B). \tag{2.3}$$

We use the following variables.

- A 2 by 2 matrix S: the overlap matrix $(\phi_i|\phi_j)$
- A 2 by 2 matrix T: the kinetic energy $(\phi_i| - \frac{1}{2}\nabla^2|\phi_i)$
- A 2 by 2 matrix Z: the matrix elements of nuclear attractions

$$(\psi| - \frac{Z_A}{|r - R_A|} - \frac{Z_B}{|r - R_B|}|\psi) \tag{2.4}$$

- A 2 by 2 by 2 by 2 tensor $\hat{V}$: the array to hold two-electron integrals V_{ijkl}.
- A 2 by 2 matrix P_σ: the density matrix for $\sigma = \alpha, \beta$
- A 2 by 2 matrix F_σ: the Fock matrix for $\sigma = \alpha, \beta$

For the last three items in the above, we use the following definitions.

$$V_{ijkl} = \int dr_1 \int dr_2 \phi_i(r_1, R_i)\phi_j(r_1, R_j)\frac{1}{|r_1 - r_2|}\phi_k(r_2, R_k)\phi_l(r_2, R_l) \tag{2.5}$$

$$\begin{aligned}
\hat{V}_{1,1,1,1} &= V_{1111} \\
\hat{V}_{2,1,1,1} &= V_{2111} \\
\hat{V}_{1,2,1,1} &= V_{2111} \\
\hat{V}_{1,1,2,1} &= V_{2111} \\
\hat{V}_{1,1,1,2} &= V_{2111} \\
\hat{V}_{2,1,2,1} &= V_{2121} \\
\hat{V}_{1,2,2,1} &= V_{2121} \\
\hat{V}_{2,1,1,2} &= V_{2121} \\
\hat{V}_{1,2,1,2} &= V_{2121} \\
\hat{V}_{2,2,1,1} &= V_{2211} \\
\hat{V}_{1,1,2,2} &= V_{2211} \\
\hat{V}_{2,2,2,1} &= V_{2221} \\
\hat{V}_{2,2,1,2} &= V_{2221} \\
\hat{V}_{2,1,2,2} &= V_{2221} \\
\hat{V}_{1,2,2,2} &= V_{2221} \\
\hat{V}_{2,2,2,2} &= V_{2222}
\end{aligned}$$

$$P^{\alpha} = \begin{pmatrix} x^2 & xy \\ xy & y^2 \end{pmatrix} \tag{2.6}$$

$$P^{\beta} = \begin{pmatrix} v^2 & vw \\ vw & w^2 \end{pmatrix} \tag{2.7}$$

$$G^{\sigma}_{ij} = \sum_{k,l} \hat{V}_{i,j,k,l} \cdot (P^{\alpha}_{k,l} + P^{\beta}_{k,l}) - \hat{V}_{i,l,j,k} \cdot P^{\sigma}_{k,l}, \tag{2.8}$$

and

$$F^{\sigma}_{i,j} = H_{i,j} + G^{\sigma}_{i,j}, \tag{2.9}$$

where $\sigma = \alpha, \beta$.

The total energy is given by

$$E_{tot} = E_{el} + \frac{Z_A Z_B}{R}, \tag{2.10}$$

and

$$E_{el} = \frac{1}{2}\sum_{i,j,\sigma} P^{\sigma}_{i,j}\left(H_{i,j} + F^{\sigma}_{i,j}\right). \tag{2.11}$$

The normalization conditions of the wavefunctions are given by

$$(x, y)S\begin{pmatrix} x \\ y \end{pmatrix} = 1, \tag{2.12}$$

and

$$(v, w)S \begin{pmatrix} v \\ w \end{pmatrix} = 1. \tag{2.13}$$

Then we proceed as follows.

- Substitute concrete values of Z_A, Z_B, the exponents, and the coefficients of STO-nG into the formulas, while other variables (R, x, y, u, w) are left as indeterminate ones. We obtain the analytical representation of the total energy.
- Transform the formula of the total energy into a polynomial through Taylor expansion at a fixed point R_0 on R and get a polynomial with real numbered coefficients. We denote it by $E_{TS}(x, y, u, v, R)$. Similarly, get polynomial representations for the normalization conditions of the wavefunctions for α and β spins. We denote the latter by $N^{\alpha}_{TS}(x, y, R)$ and $N^{\beta}_{TS}(v, w, R)$
- Introduce the Lagrange multiplier e and f and define the objective function by $F(x, y, v, w, e, f, R) = E_{TS} - e \cdot N^{\alpha}_{TS} - f \cdot N^{\beta}_{TS}$.
- The coefficients of F are real numbers. To guarantee rigorous accuracy through symbolic computation, we should replace them with integers. We multiply F by a power of ten and round down the real numbers after the decimal point.
- Differentiate the objective function with respect to indeterminate variables and get the set of polynomial equations.

For the RHF case, the formulas are composed similarly. We use the relations: $(u, v) = (x, y)$, $P^{\beta} = P^{\alpha}$, $F^{\beta} = F^{\alpha}$, $G^{\beta} = G^{\alpha}$, $N^{\beta}_{TS} = N^{\alpha}_{TS}$ and $f = e$ so that we define the objective function by $F(x, y, e, R) = E_{TS} - 2e \cdot N_{TS}$.

3 Symbolic-numeric computation to get the electronic structure

In the symbolic-numeric computations, we go through the same path as in [10].

- From the set of polynomials prepared in the previous section, we compute the Gröbner bases of lexicographic order. We execute the symbolic computation in the ring of integer coefficients. It might be better to use another monomial ordering because it would be faster in computation. Then one would apply the FGLM algorithm [8] to transform the ordering into the lexicographic one.
- Apply the triangulation of Gröbner bases and solve the equation numerically in the ring of real-numbered coefficients.

For the RHS case, we get the objective function:

```
OBJ=-782*R**4*x**3*y - 1034*R**4*x**2*y**2 - 1036*R**4*x**2
- 1037*R**4*x*y**3 + 1799*R**4*x*y + 187*R**4*y**2 + 2633*R**4
+ 4977*R**3*x**3*y + 3982*R**3*x**2*y**2 + 8767*R**3*x**2
+ 6383*R**3*x*y**3 - 10588*R**3*x*y - 303*R**3*y**2 - 19754*R**3
- 6472*R**2*x**3*y + 5751*R**2*x**2*y**2 - 30430*R**2*x**2
- 9875*R**2*x*y**3 + 6621*R**2*x*y - 5877*R**2*y**2 + 59259*R**2
- 19598*R*x**3*y - 47149*R*x**2*y**2 + 54517*R*x**2
- 12230*R*x*y**3 + 75627*R*x*y + 29906*R*y**2 - 88889*R
- 2*e*(-419*R**4*x*y + 3017*R**3*x*y - 6319*R**2*x*y
- 2791*R*x*y + 10000*x**2 + 19093*x*y + 10000*y**2 - 10000)
+ 13071*x**4 + 48009*x**3*y + 68137*x**2*y**2 - 90397*x**2
+ 36259*x*y**3 - 153801*x*y + 7746*y**4 - 65726*y**2 + 66666.
```

From this, we get the set of polynomial equations. The polynomials f[1],f[2],f[3], and f[4] are generated by the differentiation of the objective function with respect to x, y, e, and R. We use the expression by Singular [4]: in the power products, the exponents are given by integers just after the symbols. For example, an expression such as -3128x3yR3 should be read as -3128*x^3*y*R^3.

```
f[1]:
   -3128x3yR3-4136x2y2R3-4148xy3R3+14931x3yR2+11946x2y2R2+19149xy3R2
   +3352xyeR3-12944x3yR+11502x2y2R-19750xy3R-18102xyeR2-4144x2R3
   +7196xyR3+748y2R3-19598x3y-47149x2y2-12230xy3+25276xyeR+26301x2R2
   -31764xyR2-909y2R2+5582xye-60860x2R+13242xyR-11754y2R+10532R3
   +54517x2+75627xy+29906y2-59262R2+118518R-88889

f[2]:
   838xyR4-6034xyR3+12638xyR2+5582xyR-20000x2-38186xy-20000y2+20000

f[3]:
   -782x3R4-2068x2yR4-3111xy2R4+4977x3R3+7964x2yR3+19149xy2R3+838xeR4
   -6472x3R2+11502x2yR2-29625xy2R2-6034xeR3+1799xR4+374yR4-19598x3R
   -94298x2yR-36690xy2R+12638xeR2-10588xR3-606yR3+48009x3+136274x2y
   +108777xy2+30984y3+5582xeR+6621xR2-11754yR2-38186xe-40000ye+75627xR
   +59812yR-153801x-131452y

f[4]:
   -2346x2yR4-2068xy2R4-1037y3R4+14931x2yR3+7964xy2R3+6383y3R3+838yeR4
   -19416x2yR2+11502xy2R2-9875y3R2-6034yeR3-2072xR4+1799yR4-58794x2yR
   -94298xy2R-12230y3R+12638yeR2+17534xR3-10588yR3+52284x3+144027x2y
   +136274xy2+36259y3+5582yeR-60860xR2+6621yR2-40000xe-38186ye+109034xR
   +75627yR-180794x-153801y
```

It is a time-consuming task to generate the Gröbner basis of the ideal I0=(f[1],f[2],f[3],f[4]). Instead, one can replace f[4] (the optimization condition for R) with f[5]=$100 \cdot R - 146$, so that the R should be fixed at a value. At first, we work in the ring $\mathbb{Z}[x, y, R, e]$ of the degree reverse lexicographic ordering with $x > y > R > e$ because this monomial ordering enables us to compute Gröbner bases rapidly. We prepare the ideal I as follows.

```
I[1]=100R-146

I[2]=-2346x2yR4-2068xy2R4-1037y3R4+14931x2yR3+7964xy2R3+6383y3R3
+838yeR4-19416x2yR2+11502xy2R2-9875y3R2-6034yeR3-2072xR4+1799yR4
-58794x2yR-94298xy2R-12230y3R+12638yeR2+17534xR3-10588yR3+52284x3
+144027x2y+136274xy2+36259y3+5582yeR-60860xR2+6621yR2-40000xe
-38186ye+109034xR+75627yR-180794x-153801y

I[3]=-782x3R4-2068x2yR4-3111xy2R4+4977x3R3+7964x2yR3+19149xy2R3
+838xeR4-6472x3R2+11502x2yR2-29625xy2R2-6034xeR3+1799xR4+374yR4
-19598x3R-94298x2yR-36690xy2R+12638xeR2-10588xR3-606yR3+48009x3
+136274x2y+108777xy2+30984y3+5582xeR+6621xR2-11754yR2-38186xe
-40000ye+75627xR+59812yR-153801x-131452y

I[4]=838xyR4-6034xyR3+12638xyR2+5582xyR-20000x2-38186xy
-20000y2+20000
```

From the ideal I, we get the Gröbner basis SI in degree reverse lexicographic monomial ordering, shown below. The lengthy integer coefficients are abbreviated, while the power products of the variables (xy, y2, e2, and so on) are faithfully recorded.

```
SI[1]=50R-73
SI[2]=14139961485244...896614288073601619xy
+3780975798828566366...961173352539062500y2
-5085368678636127527...933593750000000000e2
-1001603465047829262...003906250000000000e
-3434041608592875777...452435883750000000000
SI[3]=30165251168521...794438145570167872x2
+2287830791971866817...747500665595656831y2
+9800854311720465164...651202059100000000e2
+1930355547334856052...468878133860000000e
+3601783924849742950...688095644737250000000
SI[4]=12272113878047...995000000000000000e3
-9278947466890114698...263392067138650177y2
+3485269694547254105...542045093600000000e2
+2997339854397009440...974353988810000000e
+9102483014928898673...129466002913500000000
SI[5]=30106893964785...092540383000000000ye2
+6583664909804927960...399718493462500000xe
+4096722245974589325...234800060784312322ye
+7284662346106449105...2724367043378169732x
+1180186413400489004...6564058109050399231y
SI[6]=18816808727991...005783773937500000xe2
+4352852234527109287...535234860661708014xe
+2838801409079480521...916529204862500000ye
+3115374855202277374...1070875685871723597x
+2240933612462673811...5264773401826784422y
SI[7]=23566602475407...012266936500000000y2e
+1965485251085135028...873838114649359991y2
+1697918650085873984...945312500000000000e2
+2618881215582933602...841094856250000000e
+4943545636472134291...941014895937500000000
SI[8]=57815402373877...342631947248598441y3
-1209549779387565779...519859020237500000xe
-2809578379906795490...109072218274832334ye
-2494722609540191577...5544991013988376604x
-3228951405017855155...3097897433756282457y
```

Using the FGLM method, we transform the basis SI into a new Gröbner basis j in lexicographic monomial ordering, which is shown below. Take note of the feature of the polynomials: j[1] includes only one variable R; j[2] includes e; j[3] includes (e,y); j[4] includes (e,y,x). We can determine R by j[1] and e by j[2]. Substituting e in j[3], we determine y from the polynomial of one variable. Similarly, by the substitution of (e,y), we determine x by j[4]. In other words, the Gröbner basis j is the result of triangulation with respect to the arrangement of variables; it contains four variables and the same number of polynomials. (To be precise, the polynomials j[2]–j[4] would include R; however, R is uniquely determined from the linear polynomial j[1] and is trivially eliminated from the other polynomials.) In general, the Gröbner basis of lexicographic monomial ordering would not exactly achieve triangulation in itself, for it might contain more number of polynomials than that of variables – even if the polynomials are arranged in such a way that the polynomial coming later shall include a wider range of variables than the polynomials coming earlier do. In such cases, we resort to primary ideal decomposition to generate several subsets of polynomials, each of which attains the triangulation. The obtained Gröbner basis j is bloated enormously in integer coefficients. For the sake of brevity, we rewrite it using decimal numbers:

```
j[1]=50*R-73
j[2]=0.32546359543271216179e+110*e4+0.11957546526364418935e
+111*e3+0.15835313702445794059e+111*e2+0.93171646353491856679e
+110*e+0.20184956174764185 06e+110
j[3]=0.92789474668901146989e+220*y2-0.12272113878047188795e
+222*e3-0.34852696945472541054e+222*e2-0.29973398543970094406e
+222*e-0.91024830149288986731e+221
j[4]=0.10585258284464530396e+244*x-0.34283892042708711652e
+244*ye3-0.12216573931889300904e+245*ye2-0.10488364636905783834e
+245*ye-0.20673267158033923667e+244*y
```

Using the Gröbner basis j, one could get the numerical solutions in Table 1, where the ground and excited states are obtained in a single run.

R	x	y	e	E$_{total}$	
1.46	0.8015	0.3371	-1.5997	-2.8627	Ground state
1.46	0.6039	-1.1152	-0.5379	-0.4737	Excited state

Table 1: The list of RHF solutions. There are also solutions with inverted signs (R,-x,-y,e) with respect to the wave function components (x, y), but they are omitted.

Similarly, one could get the solutions of the UHF model, which are shown in Table 2.

R	x	y	v	w	e	f	E$_{total}$	
1.46	-0.8013	-0.3373	-0.8013	-0.3373	-1.6003	-1.6003	-2.8636	Ground state
1.46	0.6041	-1.1152	0.6041	-1.1152	-0.5377	-0.5377	-0.4739	Excited state
1.46	0.9096	0.1734	0.8310	-1.0464	-1.8824	-0.5897	-1.8958	Excited state

Table 2: The list of UHF solutions. The complex-valued solutions are omitted since they are absurd. There are also solutions with inverted signs of the wavefunction components. In addition, there are solutions where (x,y,e) and (v,w,f) are interchanged due to the symmetry of the spins. Those redundant solutions are omitted.

4 How the triangulation works to get eigenstates

In the example above, the efficacy of triangulation is obscure. Let us compute another example (the UHF of H2), using STO-3G. We compute the Grönber basis of the polynomials whose roots give the local minima of the energy functional. Working in the lexicographic monomial orderings, we get a triangulation that is decomposed into two triangular sets through Moller's algorithm [16].

In the below, we show two resulting triangular sets (T[1] and T[2]), each of which includes seven polynomials (_[1],..._[7]). In the presented polynomials, the length integer coefficients are abbreviated, while the power products of the variables are faithfully recorded. The tangible difference lies in the third polynomials in these two sets: T[1]_[3] is e-f, while T[2]_[3] is more complicated. It means that the former represents the quantum state where the two electrons with different spins have equal orbital energy, while the latter represents the state lacking in such a symmetric feature. We have successfully decomposed the equation into different subsets which give different electronic configurations.

```
T[1]: The first triangular set.
   _[1]=5R-7
   _[2]=801399222030...170032137001335625f2
   +3043462323791652...8701746433379249346f
   -1271909255306394...64711461694927766603
   _[3]=e-f
   _[4]=124265968727...963754965612968924w4
   -1626966225314171...90339173830057533w2f
   -5486085686194680...604030872578693149w2
   +1739854071254451...241213112500000000f
   +8537297330291821...9484217881250000000
   _[5]=399943914650...2697665231318750000v
   -1234497384567144...53282985876224375w3f
   -1468437643427458...924954485246719547w3
   +1234497384567144...153282985876224375wf
   +6739370164557969...7353267035762645404w
   _[6]=621944877024...669665030789398808y2
   -3205596888121015...80128548005342500w2f
   -6086924647583305...403492866758498692w2
   -9801053048616961...1739909708522223125f
   +4051900478244171...73320854416630935169
   _[7]=513331214005...4905719466175000000x
   +5792959023903118...8724869774795000yw2f
   -1974205463586649...74770597342356624yw2
   +2246059961750649...686566455420870625yf
   +8622685126305071...7359601249754719375y

T[2]: The second triangular set.
   _[1]=5R-7
   _[2]=610729994390...092845856727498721f4
   +4658149845705284...034411595989026052f3
   -5680360790681349...251982271043873858f2
   -5566291054774740...2367043024020291084f
   +8593637453448086...77349315653555217769
   _[3]=147725437365...9490443785400000000e
   +1017755035287551...400806093509475833f3
   -2592019554047912...251283850363855229f2
   -3684750207917733...6045163863486752073f
   +7978230722523506...45439898622626274509
   _[4]=654311505104...723696396630434131w2
   +3112891080506857...600843916534765625f3
   +1780171830853346...750573460316796875f2
   -1112543953229220...9191887189737890625f
   -8339344332146638...96529825162969921875
   _[5]=115158824898...1370565806956407056v
   -9407852666005712...39743338549262047wf3
```

```
-5380077192458336...76704351486875773wf2
+3362356512240005...930356958574916247wf
+7727490576779581...8260831914283439029w
_[6]=430022542773...686670821540182848y2
+4645726947773738...974360298304433313f3
-1014075517163233...839728775946966469f2
-1616557538344848...6000954092094883953f
+2933360528129523...82831318262444742549
_[7]=295640498156...8980887570800000000x
-5484541128828930...67709118342972759yf3
+1197173003093830...97269419559522067yf2
+1908436807810983...809150269238934279yf
-3911644380907348...3708961991460941507y
```

5 Solution by eigenvalue problem

We can solve sets of polynomial equations through eigenvalue problems in linear algebra [17]. The application of this algorithm to quantum chemistry is demonstrated in this section.

Let I be a polynomial ideal defined in a ring R. We can get the monomial basis in the factor ring R/I with the aid of Gröbner basis of I. In the aforementioned RHF model of HeH+, we get the monomial basis as follows.

$$Q_{base} = \begin{pmatrix} ye^3, \\ ye^2, \\ ye, \\ y, \\ e^3, \\ e^2, \\ e, \\ 1 \end{pmatrix}$$

We can compute the product between an arbitrary monomial p and Q_{base} in R/I. This is a linear transformation (by a matrix M_p) on Q_{base}:

$$p \cdot Q_{base} = M_p \cdot Q_{base}. \tag{5.1}$$

Even if p≠q, it is guaranteed that

$$M_p \cdot M_q = M_q \cdot M_p. \tag{5.2}$$

In other words, any pair of such transformation matrices are commutable with each other, and they share common eigenvectors. The eigenvalues of M_p give the numerical data of p in the roots of the set of polynomial equations defined by the ideal I:

$$M_p V_{eig} = w_p V_{eig}. \tag{5.3}$$

From this eigenvector, we can compute the numerical data of other monomials $q(\neq p$ by

$$w_q = \frac{(V_{eig}^*, M_q \cdot V_{eig})}{(V_{eig}^*, V_{eig})}. \tag{5.4}$$

In this way, we get the solutions to the set of non-linear polynomial equations by linear solvers. If we look at this matter in another light, it means that we can solve the non-linear Hartree-Fock model by applying the eigenvalue problem only once.

Let us investigate the RHF model of HeH+ by this method. The transformation matrices (M_x, M_y, M_e, M_R) for variables (x, y, e, R) are given below, from which we get the numerical solutions of the quantum states, which are equivalent to the ones computed by the triangulation of the polynomial ideal.

```
Mx=
[[0, 0, 0, 0,
  11.080151325865552, -4.533316123788358,
  -0.35836894442630574, 3.2388337744224454]
 [0, 0, 0, 0,
  21.07390644331965, -5.5752716552661035,
  -5.8499651704764695, 11.541120304847897]
 [0, 0, 0, 0,
  13.19994598967836, -0.9827794471874843,
  -7.318902812741645, 9.908463596300761]
 [0, 0, 0, 0,
  2.811521428790274, 0.22225715991443362,
  -2.008695249222711, 1.953024347868306]
 [8.931697287643605, -8.397156206184581,
  6.545956632156977, -3.5365217362474493,
  0, 0, 0, 0]
 [24.310030931798412, -21.919490812550833,
  15.652716678834729, -6.447239472143048,
  0, 0, 0, 0]
 [19.979101497085832, -16.546029346336013,
  9.929624789762936, -1.5541021159188364,
  0, 0, 0, 0]
 [5.207839905693149, -4.059742766816225,
  2.1933186156303637, -0.19450451855497125,
  0, 0, 0, 0]]

My=
[[0, 0, 0, 0, 1, 0, 0, 0]
 [0, 0, 0, 0, 0, 1, 0, 0]
 [0, 0, 0, 0, 0, 0, 1, 0]
 [0, 0, 0, 0, 0, 0, 0, 1]
 [-5.535885815356438, 8.47906706551838,
  -11.030456182591696, 13.225760703827165,
  0, 0, 0, 0]
 [-17.8798032915008, 25.616243135133775,
  -32.0468764996916, 37.56104565721137,
  0, 0, 0, 0]
 [-17.43234485713924, 23.374791314708975,
  -28.052043082927877, 32.302584588309806,
   0, 0, 0, 0]
 [-5.258640275660543, 6.840988600806554,
  -8.202496498256208, 9.80982277074971,
  0, 0, 0, 0]]

Me=
[[-3.6740043108251648, 1, 0, 0, 0, 0, 0, 0]
 [-4.865463887410308, 0, 1, 0, 0, 0, 0, 0]
 [-2.8627363447398095, 0, 0, 1, 0, 0, 0, 0]
 [-0.6201909048515171, 0, 0, 0, 0, 0, 0, 0]
 [0, 0, 0, 0, -3.6740043108251648, 1, 0, 0]
 [0, 0, 0, 0, -4.865463887410308, 0, 1, 0]
```

```
 [0, 0, 0, 0, -2.8627363447398095, 0, 0, 1]
 [0, 0, 0, 0, -0.6201909048515171, 0, 0, 0]]

MR=
[[1.46, 0, 0, 0, 0, 0, 0, 0]
 [0, 1.46, 0, 0, 0, 0, 0, 0]
 [0, 0, 1.46, 0, 0, 0, 0, 0]
 [0, 0, 0, 1.46, 0, 0, 0, 0]
 [0, 0, 0, 0, 1.46, 0, 0, 0]
 [0, 0, 0, 0, 0, 1.46, 0, 0]
 [0, 0, 0, 0, 0, 0, 1.46, 0]
 [0, 0, 0, 0, 0, 0, 0, 1.46]]
```

Table 3 shows the real roots of the equation of the RHF model which are computed from different eigenvectors $\{V_i \mid i = 1,2,3,4\}$ of the transformation matrix M_y: $(V_i^*, M_p \cdot V_i)/(V_i^*, V_i)$ for $p = x, y, e, R$. It includes the computations by the eigenvectors which give real roots only. We can ascertain that the roots are computed with good precision.

	M_x	M_y	M_e	M_R
V_1	-0.8015	-0.3371	-1.5997	1.46
V_2	-0.6039	1.1152	-0.5379	1.46
V_3	0.8015	0.3371	-1.5997	1.46
V_4	0.6039	-1.1152	-0.5379	1.46

Table 3: The roots of the equation of the RHF model are computed from different eigenvectors $\{V_i \mid i = 1,2,3,4\}$ of the transformation matrix M_y. The rows and columns are indexed by the eigenvectors (V_1, V_2, V_3, V_4) and the transformation matrices M_x, M_y, M_e, M_R, respectively. The crossing of a column and a row shows the corresponding expectation value: $(V_i^*, M_p \cdot V_i)/(V_i^*, V_i)$ for $i = 1,2,3,4$ and $p = x, y, e, R$.

6 conclusion

In this article, we presented a benchmark test problem of *algebraic quantum chemistry* for the electronic structure of heteronuclear diatomic molecule HeH+, which should be solved by the Gröbner basis technique. The example in the present article is a little more complicated than that in [10], for, in the latter, the computation of H_2 (the simplest homonuclear model) through STO basis $\phi(r) \sim \exp(-r)$ was discussed. The benchmark problem in the preset article is extensible for various purposes; for example–

- In the present article, we prepared the atomic orbital by the GTO-nG model which is given by fixed numerical data, but we easily replace them with symbolic variables. Thus we could derive an analytic representation of total energy where the wavefunction, the nuclear distance, and the orbital exponents are variables. The optimization of all of those variables shall be a more complicated benchmark problem.
- Extension to molecules including more number of electrons. To this end, we should include the orthogonality of wavefunctions in the same spin.

- The GitHub of the authors of the present article [14] shows several model problems, such as the case of H3+: they cover the simple RHF or UHF computations and the simultaneous optimization of the bond length and the electronic structures, or so.

The authors of the present article invite the readers to try these problems by themselves. One of the left problems (which shall be the hardest) would be the preparation of symbolic formulas of atomic orbital integrals. In [10], the atomic orbital integrals were prepared by STO, and the mathematical difficulty to compute two-electron integrals did not allow that seminal study to proceed into the investigation of the general polyatomic molecules. The method to compute two-electron integrals in the three- or four-centered systems by STO has not yet been settled; but without them, one could not discuss the quantitative electronic structure by STO models. On the other hand, if one adopts the GTO, the hardship shall greatly be mitigated; with the use of GTO, every required atomic orbital integral could be computed and represented analytically by special functions whose natures are well-studied. Since the two-electron integrals would be computed efficiently through recursive ways, such as the Obara-Saika method and its extensions, it seems that there are no theoretical limitations; the necessary steps are to prepare the integrals of s-shells, to compute the differentials of the formulas, and to do the symbolic computations by recursive paths; if we meet some limit in symbolic computations, it would be owing to the computational resources.

Finally, we mention the possible direction of the future study. It is related to the *beyond Born-Oppenheimer* treatment. We have constructed the polynomial function of the total energy $E(x, y, R)$ that shall undergo the minimization with respect to the variables. We can re-quantize the model by mating the variables with the corresponding partial differentiation operators. For example, let us take the interatomic distance R, and assume that R is not a fixed point, but a distribution given by a probabilistic model of quantum dynamics. The modified total energy shall be represented as

$$\langle\psi(R)\left|-\frac{1}{2\mu}\frac{d^2}{dR^2}+E(R,x,y)\right|\psi(R)\rangle \tag{6.1}$$

with the *wavefunction* $\psi(R)$ defined on R, to which a virtual mass μ is assigned. One can minimize it in various ways; if $\psi(R)$ is given by a linear combination of Gaussian functions, the modified total energy is represented or approximated by a polynomial after the integration along R, because the potential term $E(R, x.y)$ is a polynomial of R according to our scheme. One can now apply the algebraic method for the optimization of this new problem. R is no longer a number as in classical dynamics; it is an operator in the sense of quantum dynamics, and it is evaluated by the expectation $\langle\psi|R|\psi\rangle$. This composition shall allow us to set foot in the realm of the *beyond Born-Oppenheimer* theory.

Appendix

The supplementary materials (including the small programs used in the study and the result of the computations) are available from our GitHub [14]:

`http://github.com/kikuchiichio/AlgebraicQuantumChemistry`

`http://github.com/kikuchiichio/AlgebraicQuantumChemistry/supplement-HeH+-computation.tex`

The small programs include the functions to compute the molecular integrals by Cartesian GTO basis

$$\phi_\alpha(r, A) = \exp(-\alpha|r - A|^2) \tag{6.2}$$

from which the following integrals are analytically derived:

$$S_{ab} = \int dr\, \phi_a(r, A)\phi(r, B), \tag{6.3}$$

$$K_{ab} = \int dr\, \phi_a(r, A) \left(-\frac{1}{2} \nabla^2 \right) \phi_b(r, B), \tag{6.4}$$

$$(\phi_a | 1/r_c | \phi_b) = \int dr\, \phi_a(r, A) \frac{1}{|r - C|} \phi_b(r, B), \tag{6.5}$$

$$[\phi_a \phi_b | \phi_c \phi_d] = \int dr_1 \int dr_2\, \phi_a(r_1, A) \phi_b(r_1, B) \frac{1}{|r_1 - r_2|} \phi_c(r_1, D) \phi_d(r_1, D). \tag{6.6}$$

In the above, the coordinates are given in the three-dimensional Cartesian system: $r = (x, y, z)$. The capital letters (A, B,...) represent the positions of the distinct atoms.

The above integrals belong to a subclass of analytic integrals which involve primitive Cartesian Gaussian functions

$$\phi_\alpha^{ijk}(r, A) = (x - A_x)^i (x - A_y)^j (z - A_z)^k \exp(-\alpha |r - A|^2). \tag{6.7}$$

As Boys has commented, we can easily derive the formulae for the general cases by differentiation with respect to the parameters in the integral formulae, followed by taking the appropriate linear combinations [1]. This opinion might be a bit optimistic because symbolic differentiation would sometimes be a demanding task for computers. However, if we meet difficulty in the symbolic differentiation to generate molecular integrals, we could use recursive methods, such as Obara-Saika or so. We should keep in mind this point: in our method, we utilize the polynomial approximation of molecular integrals, and, for this purpose, symbolic differentiation is an indispensable tool. If the symbolic differentiation is not practicable on account of complexity, then the problem we are challenging would be a hard one beyond the limitation of available computational resources; we should restate the problem into an easier form.

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